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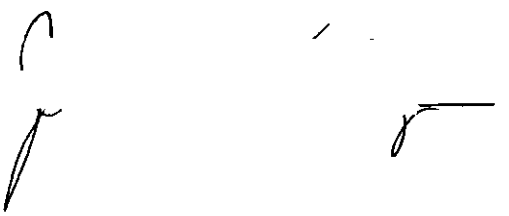

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OXYGEN BRIDGED COMPLEXES OF SOME TRANSITION METAL IONS

A THESIS

Presented to

The Faculty of the Division of Graduate

Studies and Research

by

James Alton Kelley

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OXYGEN BRIDGED COMPLEXES OF SOME TRANSITION METAL IONS

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SUMMARY

The preparation, magnetic properties, spectral properties, crystal and molecular structure of some transition metal oxygen-bridged complexes have been investigated; correlations between the observed properties and structures have been made in terms of current bonding theories.

This thesis reports the preparation of several new μ_4-oxo complexes with the general formula $M_4OX_6L_4$. The crystal and molecular structures of two of these complexes are reported. The $Cu_4OCl_{10}^{-4}$ anion and $Cu_4OBr_6(NH_3)_4$ have structures similar to those of other reported complexes of this type, that is, four copper(II) atoms tetrahedrally surrounding a central oxygen atom with each pair of copper atoms being bridged by a halogen atom. The halogen atoms above the six edges of the tetrahedron form a regular octahedron around the central oxygen. A partial structure of $Cu_4OBr_6(TPPO)_4 \cdot 2CH_3NO_2$ indicated that the structure is essentially the same as that of $Cu_4OCl_6(TPPO)_4$. The preparation of the μ_4-oxo complexes $Cu_4O(acetate)_6$ and $Cd_4OCl_{10}^{-4}$ are also reported.

Other complexes chosen for study were the dianions of the mono-Schiff's bases of acetylacetone and 2-aminoethanol, Cu(EIA); 3-amino-1-propanol, Cu(PIA), and the copper(II) chloride complex of the anion of the Schiff's base of salicylaldehyde and 3-amino-1-propanol, Cu(SALPA)Cl. The two complexes with subnormal magnetic moments, Cu(PIA)

and Cu(SALPA)Cℓ, have planar coordination for the bridging oxygens, a feature consistent with π-bonding. The complexes with normal magnetic moments, Cu(EIA) and the μ_4-oxo complexes, have tetrahedral coordination for the bridging oxygen(s); no π-system can be present since all of the outer orbitals on the bridging oxygen(s) were used in σ-bonding. The effect of a σ-interaction on the magnetic exchange is unknown but seems to be minimal as the magnetic moments of Cu(EIA) and the μ_4-oxo compounds indicate. The effect of metal-metal bonding on the magnetic exchange also seems to be minimal since the copper-copper distances are the same in Cu(PIA) and Cu(EIA) even though the magnetic moments differ significantly; the copper-copper distance in Cu(SALPA)Cℓ is longer than that in Cu(EIA), yet the magnetic moment of Cu(SALPA)Cℓ is subnormal while that of Cu(EIA) is normal. On the basis of these results, the most effective mechanism for magnetic exchange in these complexes is a π-interaction.

The preparation, crystal and molecular structure of a trinuclear cobalt complex, bis{tris(2-aminoethoxido)cobalt(III)} cobalt(II), are also reported. The trigonal prismatic coordination of the central cobalt(II) atom provided the first example of this type of coordination with oxygens as donor atoms. This suggests that there may be a significant energy minimum corresponding to trigonal prismatic coordination.

CHAPTER I

INTRODUCTION

Although a number of oxygen-bridged transition metal complexes are known, there have been few systematic attempts to prepare and study such compounds. At the time this work was begun, there was little understanding of the conditions which favored the formation of such compounds--most of the compounds had been prepared and isolated accidentally. Some complexes with oxygen bridges are known to catalyze certain organic reactions, others exhibit unusual magnetic properties; in spite of these properties, there have been only scattered attempts to relate structures and bonding to the properties of these compounds. The purpose of this work was (1) to prepare oxygen-bridged complexes of transition metal ions, (2) to investigate the magnetic properties, spectral properties, and crystal and molecular structures of these compounds, and (3) to attempt, on the basis of current bonding theories, to relate the observed properties and structures.

There has been considerable interest in oxygen-bridged complexes with subnormal magnetic moments (1)--moments lower than would be predicted on the basis of ligand field theory. When the distance between adjacent metal atoms is sufficiently large to rule out metal-metal bonding, the lowering of the magnetic moment has been attributed to a phenomenon called super-exchange. Super-exchange has been used to explain the subnormal magnetic moments in a variety of different types

of compounds, such as copper(II) formate tetrahydrate (μ = 1.64 B.M.) and copper(II) oxide (μ = 0.78 B.M.).

The structure of copper(II) formate tetrahydrate (1) can be described as an infinite lattice network of copper ions bridged by formate ions. Martin (1) has suggested that the pathway for super-exchange is through a π-interaction--the π-interaction being between the copper d_{xz} and d_{yz} orbitals and the π-system on the formate ions. This interaction would extend throughout the entire lattice. However, a different explanation is necessary to explain the super-exchange mechanism in copper(II) oxide (1). The copper(II) oxide structure (2) is also an extended-type with square planar copper ions and tetrahedral oxygen ions, but there cannot be an extended π-type interaction throughout the lattice as in copper(II) formate tetrahydrate since all of the outer orbitals of the oxygen atoms have been used in σ-bonding and none remain for π-bonding. Thus, the mechanism for super-exchange in CuO has been considered to be a σ-type interaction extending throughout the lattice. Since current bonding theories cannot adequately explain the bonding in extended structures in such a way to account for the magnetic properties, it is more feasible to study simpler systems that show the same type of magnetic properties and have the same basic structural units, except in a non-extended form, with the hope that the results can be related back to the extended lattice compounds. There are examples of such systems and these are usually polynuclear complexes with less than about six metal atoms per polynuclear unit.

In attempts to explain the mechanism for magnetic interaction in complex molecules, the energies of the different paths for the exchange process must be considered. If the distance between adjacent metal atoms is very close to that found in the free metal, metal-metal bonding must be considered as a possible explanation for the interaction. However, if metal-metal bonding can be ruled out on the basis of metal-metal distances or comparison of other structural features, other mechanisms must be considered. There are two remaining possibilities, a σ-interaction through the σ-framework or a π-interaction through a π-system. The absolute energies of the σ and π paths cannot normally be found easily, but one of the two possibilities can usually be chosen on the basis of structural information. For example, the unusual magnetic properties of the Ru(IV) complex, $Ru_2OCl_{10}^{-4}$ (3), which is diamagnetic, have been explained on the basis of a multicenter bonding interaction. The multicenter interaction, two π bonds and one σ bond between each Ru atom and the bridging oxygen, is consistent with a linear Ru-O-Ru arrangement (4). Also on the basis of structural information, explanations for the sub-normal magnetic moments of the basic acetates of Cr(III) and Fe(III), $M_3O(acetate)_6Cl\cdot 5H_2O$ (5,6), have been offered. Figgis, et al., have suggested that the magnetic interaction occurs through the M-O-M linkage at the central oxygen since the metal-metal distances are large, 3.28Å for Cr(III).

Since a structural approach had led to reasonable explanations for the magnetic properties of $Ru_2OCl_{10}^{-4}$ and the basic acetates of Cr(III) and Fe(III) in terms of current bonding theories and since there

was little structural information available for oxygen-bridged copper(II) complexes exhibiting unusual magnetic properties, an investigation of the structural and magnetic properties of oxygen-bridged copper(II) complexes seemed promising.

One type of oxygen-bridged copper(II) complex known is the pyridine-N-oxide (PyO) complex of copper(II) chloride (7), $CuCl_2(PyO)$. This complex is dimeric with bridging oxygen atoms from the pyridine-N-oxide molecules. Since metal-metal bonding can be ruled out on the basis of a long copper-copper distance, 3.23Å, either a σ-interaction or a π-interaction is responsible for the subnormal magnetic moment (μ = 0.85 B.M.) and both have been offered as explanations. Another type of oxygen-bridged copper(II) complex with a subnormal magnetic moment (μ = 1.37 B.M.) is the complex of the dianion of the mono-Schiff's base formed between acetylacetone and o-hydroxyaniline (8). The tetrameric units of this complex are built up by the copper atoms of one "dimer" coordinating to the bridging oxygen atom (phenolic oxygen) of another "dimer". There are two of this type of Cu-O bonds in each tetramer.

In contrast to the two oxygen-bridged copper(II) complexes described above which had subnormal magnetic moments, Bertrand (9,10) prepared a new type of polynuclear oxygen-bridged complex of copper(II) with a normal magnetic moment (μ = 2.2 B.M.). This complex was prepared in an attempt recrystallize dichlorobis(triphenylphosphine oxide) copper(II), $CuCl_2(TPPO)_2$, from methylisobutyl ketone. Only a small quantity of this material was obtained by this method, but enough was

available for carbon and hydrogen analysis and for an X-ray structure determination. When the $CuCl_2(TPPO)_2$ was refluxed in methylisobutyl ketone, the initial yellow color changed to orange. Well-formed, red crystals of μ_4-oxo-hexa-μ-chlorotetrakis{triphenylphosphine oxide copper(II)}, $Cu_4OCl_6(TPPO)_4$, were deposited over a period of several days. The crystals were cubic, a = 12.22Å, with one molecule per unit cell and of space group symmetry $P\bar{4}3m$. A three-dimensional X-ray crystal structure found the structure to be as shown in Figure 1.

The central oxygen atom, O(1), is at the center of a regular tetrahedron of copper atoms with a Cu-O(1) distance of 1.90Å. Between each pair of copper atoms, there is a bridging chlorine atom with a Cu-Cl distance of 2.38Å. The six chlorine atoms form an octahedron around the central oxygen atom, O(1). Each copper atom is on a three-fold axis and the three chlorine atoms coordinated to each copper atom are related by this threefold axis. The copper atom is displaced 0.23Å from the plane of these three chlorine atoms, and away from the central oxygen to give a Cl-Cu-O(1) angle of 85°. Completing a slightly distorted trigonal bipyramid around the copper atom is the oxygen atom of the triphenylphosphine oxide (TPPO), O(2). The Cu-O(2) distance is 1.89Å. Since the Cu, O(2) and the P lie on a threefold axis, the bond angle at O(2) is 180°. The Cu-Cu distance is 3.11Å.

Since magnetic interaction between copper atoms in polynuclear copper(II) complexes with oxygen bridges is usually found (1), the room temperature magnetic moment of 2.2 Bohr magnetons for this complex is unusual. However, this value is only slightly greater than that

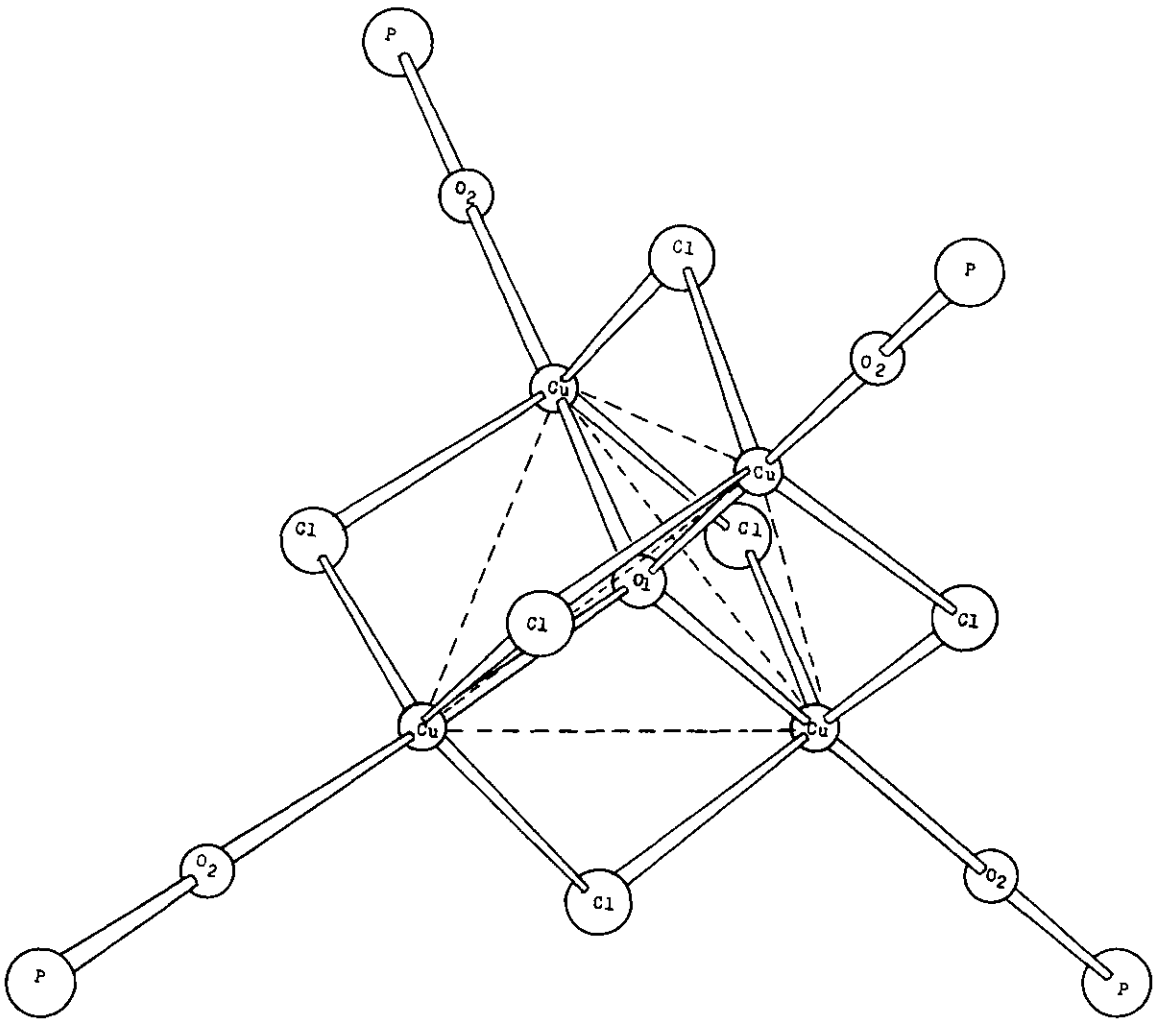


Figure 1. Perspective Drawing of the Structure of μ_4-oxo-hexa-μ-chloro-tetrakis{(triphenylphosphine oxide)copper(II)}

predicted for a trigonal bipyramidal copper(II) atom (11). The visible and near infrared spectrum of this complex is similar to that reported for the trigonal-bipyramidal $CuCl_5^{-3}$ (12,13). $Cu_4OCl_6(TPPO)_4$ shows absorption bands at 9.9 kilo Kaisers (kK) and 11.2 kK and $CuCl_5^{-3}$ shows absorption bands at 8.2 kK and 10.4 kK.

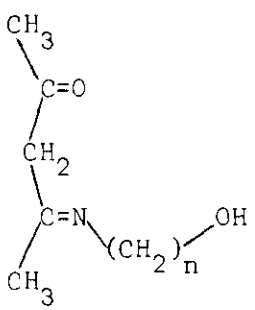
The infrared spectrum of Bertrand's compound also showed an interesting feature (9,10). The phosphorous-oxygen stretching frequency (1194 cm^{-1}) is at a much higher energy than that reported for other phosphine oxide complexes (14). Bertrand attributes this increase to π-bonding between the copper and oxygen atom of the phosphine oxide. This π-bonding argument was also substantiated by the linear Cu-O(2)-P arrangement.

Since Bertrand's initial preparation of $Cu_4OCl_6(TPPO)_4$ resulted in a poor yield, better synthetic paths to this compound were desirable. The results of the development of better synthetic routes to this complex are reported in this thesis.

This thesis will also report the preparation of several new compounds with the general formula $M_4OX_6L_4$, where M is other transition metal ions with a plus two oxidation state, X is a halogen and L is other ligands replacing the TPPO. Such preparations seemed feasible since it was known that $Mg_4OBr_6(C_4H_{10}O)_4$ (15) had a structure similar to $Cu_4OCl_6(TPPO)_4$. The magnetic and spectral properties of these new compounds will also be reported. X-ray crystal structures for two of these compounds will be reported.

During the course of this work, Bock, et al. (16) reported the preparation of several compounds similar to $Cu_4OCl_6(TPPO)_4$. They reported forming several copper(II) complexes with the general formula $Cu_4OX_6L_4$ where X = Cl or Br and L is an aromatic amine. Dunitz (17) reported the X-ray crystal structure of one of these compounds, $Cu_4OCl_6(pyridine)_4$. The basic arrangement of the atoms was the same as that of $Cu_4OCl_6(TPPO)_4$, but the octahedron of chlorine atoms was quite distorted in the pyridine complex. This distortion was attributed to intermolecular repulsions within the crystal lattice.

This thesis will also report the preparation, magnetic and spectral properties, and X-ray crystal structures of two oxygen-bridged copper(II) complexes of a different type. The compounds were formed using the Schiff's bases shown below,



where n = 2 and 3. The Schiff's bases were formed by the reaction of acetylacetone with the appropriate aminoalcohol. Correlations between the magnetic properties and solid state structures of these two complexes will be presented. The magnetic properties and spectral properties and crystal and molecular structure of a new dimeric five-

coordinate oxygen-bridged copper(II) complex, the copper(II) chloride complex of the mono-anion of the Schiff's base of salicylaldehyde and 3-amino-1-propanol, will also be presented. The structure and magnetic properties of this compound will be related to the previous compounds.

The preparation, crystal and molecular structure of a trinuclear oxygen-bridged cobalt complex will also be reported. The unusual structure and stereochemistry of this complex will be discussed.

CHAPTER II

EXPERIMENTAL

Preparation of Complexes

μ_4-oxo-hexa-μ-chlorotetrakis{triphenylphosphine oxide copper(II)} $Cu_4OCl_6(TPPO)_4$

Since Bertrand's initial preparation resulted in a very low yield of $Cu_4OCl_6(TPPO)_4$, methods of obtaining better yields were sought.

Method One. Stoichiometric amounts of anhydrous $CuCl_2$, CuO, and triphenylphosphine oxide(TPPO) were mixed in nitromethane and refluxed for about two hours; the hot solution was then filtered. Red-orange crystals slowly deposited over a period of several days. The crystals were filtered and then dried over sulfuric acid. This material was identified as being the same as Bertrand's initial material by elemental analysis and by unit cell and space group determinations. Analytical data for $Cu_4OCl_6(TPPO)_4$ are summarized in Table 1.

Method Two. Small amounts, but very large crystals, of $Cu_4OCl_6(TPPO)_4$ were prepared by mixing anhydrous $CuCl_2$ (0.01 mole) and KOH (0.003 mole) in nitromethane and then adding triphenylphosphine oxide (0.013 mole). This solution was filtered while hot and after several days large red-orange crystals, about 0.5 cm square, were deposited. The crystals were identified as being $Cu_4OCl_6(TPPO)_4$ by a unit cell determination.

Table 1. Analytical Data

	Per Cent Metal		Per Cent Halogen		Per Cent Carbon		Per Cent Hydrogen		Per Cent Nitrogen		Per Cent Phosphorous	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Cu_4OCl_6(TPPO)_4$	15.92	16.21	13.33	13.55	54.17	53.61	3.80	3.64	-	-	7.76	7.41
$Cu_4OCl_6(TPPO)_4 \cdot 2CH_3NO_2$	14.80	14.46	12.39	12.09	51.76	50.38	3.88	3.78	1.63	1.72	7.22	7.13
$[(CH_3)N]_4Cu_4OCl_{10}$	27.58	27.77	38.48	38.10	20.85	21.00	5.26	5.22	-	-	-	-
$K_4Cu_4OCl_{10}$	32.08	32.27	45.12	45.38	-	-	-	-	-	-	-	-
$Cu_4OCl_6(PyO)_4$												
Method 1	29.44	29.03	24.64	23.44	27.82	28.18	2.34	2.50	6.49	6.47	-	-
Method 2	29.44	28.33	-	-	27.82	28.33	2.34	2.48	6.49	6.25	-	-
$Cu_4OCl_6(Py)_4$	31.80	30.94	26.62	26.29	-	-	-	-	-	-	-	-
$Cu_4OBr_6(TPPO)_4 \cdot 2CH_3NO_2$	12.80	12.85	-	-	44.77	43.95	3.36	3.42	1.41	1.35	-	-
$Cu_4OBr_6(NH_3)_4$	-	-	-	-	0.00	1.67	1.48	1.64	6.85	6.83	-	-
$Cu_4O(acetate)_6$	40.70	41.07	-	-	23.08	23.12	2.91	2.98	-	-	-	-
$[(CH_3)_4N]_4Cd_4OCl_{10}$	-	-	34.87	35.46	18.90	18.74	4.76	4.54	-	-	-	-
Cu(EIA)	31.04	30.85	-	-	41.06	41.12	5.43	5.37	6.84	6.78	-	-
Cu(PIA)	29.05	28.62	-	-	43.92	44.07	6.00	5.96	6.40	6.30	-	-
Cu(mSALPA)	23.46	23.68	-	-	48.79	48.66	4.85	4.88	5.17	5.04	-	-
Cu(SALPA)Cl	22.92	22.93	-	-	43.33	43.13	4.36	4.40	5.05	5.04	-	-
"Cobalt trimer"	26.97	27.04	-	-	29.32	29.88	6.47	6.88	12.83	11.79	-	-

μ_4-oxo-hexa-μ-chlorotetrakis{triphenylphosphine oxide copper(II)} dinitromethane, $Cu_4OCl_6(TPPO)_4 \cdot 2CH_3NO_2$

In an attempt to replace the central oxygen atom in these complexes with a sulfur atom, CuS was substituted for CuO in method one above. After filtering the hot solution, orange crystals were deposited over a period of several days. It was first thought that this was the desired material, $Cu_4SCl_6(TPPO)_4$, but elemental analysis showed no sulfur was present. Elemental analysis, Table 1, and a molecular weight determination via the density and unit cell volume determination indicated that the compound was $Cu_4OCl_6(TPPO)_4 \cdot 2CH_3NO_2$. The same compound could be prepared by heating the mixture in method one above for only about 15 minutes. The two nitromethane molecules could be removed by heating the compound under vacuum in a drying pistol; recrystallization of the compound from acetone yielded unsolvated $Cu_4OCl_6(TPPO)_4$.

The Tetramethylammonium Salt of μ_4-oxo-hexa-μ-chlorotetra{chlorocuprate(II)}, $[(CH_3)_4N]_4Cu_4OCl_{10}$ (18)

A mixture of anhydrous $CuCl_2$ and CuO was refluxed in methanol for about 24 hours. The hot solution was filtered and tetramethylammonium chloride added. Deep-red octahedral-shaped crystals were slowly deposited; after one day the crystals were filtered and then dried in a vacuum dessicator over sulfuric acid. Analytical data are given in Table 1 for $[(CH_3)_4N]_4Cu_4OCl_{10}$.

Tetrapotassium μ_4-oxo-hexa-μ-chlorotetra{chlorocuprate(II)}, $K_4Cu_4OCl_{10}$

About 0.1 gram of 85 per cent KOH was dissolved in 10 ml of methanol and this solution was added to a solution which contained 0.7 gram of anhydrous $CuCl_2$ in 125 ml benzene. A red powder precipitated

immediately from the solution. The only solvent in which this material seemed to dissolve in was water, in which it decomposed. Analytical data for $K_4Cu_4OCl_{10}$ are given in Table 1.

μ$_4$-oxo-hexa-μ-chlorotetrakis{pyridine-N-oxide copper(II)}, $Cu_4OCl_6(PyO)_4$

Method One. A mixture of anhydrous $CuCl_2$ and CuO was refluxed in isobutyl alcohol for about 48 hours. This hot solution was filtered and pyridine-N-oxide (PyO) was added to the filtrate. A golden yellow, very insoluble, powder precipitated immediately. This material was washed with acetone and dried in a vacuum dessicator. Analytical data for $Cu_4OCl_6(PyO)_4$ are given in Table 1.

Method Two. Pyridine-N-oxide was added to a solution of $Cu_4OCl_6(TPPO)_4$ in acetone and a golden yellow powder precipitated immediately. Analytical data for this method are summarized in Table 1.

μ$_4$-oxo-hexa-μ-chlorotetrakis{pyridine copper(II)}, $Cu_4OCl_6(Py)_4$

Since the preparation of $Cu_4OCl_6(Py)_4$ by Bock (16) gave very small yields, a preparation giving better yields was developed. Anhydrous $CuCl_2$ and CuO were refluxed in isobutyl alcohol for about 48 hours. The hot solution was filtered and pyridine added. A golden-yellow, very insoluble, powder was precipitated immediately. The compound was washed with acetone and dried in a dessicator. Analytical data for $Cu_4OCl_6(Py)_4$ are given in Table 1.

μ$_4$-oxo-hexa-μ-bromotetrakis{triphenylphosphine oxide copper(II)} dinitromethane, $Cu_4OBr_6(TPPO)_4 \cdot 2CH_3NO_2$

A 3:1 molar ratio of $CuBr_2$ (0.01 mole) and KOH (0.003 mole) was dissolved in nitromethane and then triphenylphosphine oxide (TPPO)

(0.013 mole) was added. The hot solution was filtered and deep-red crystals formed in about one day. The crystals were filtered and then dried in a vacuum dessicator over sulfuric acid. Analytical data for $Cu_4OBr_6(TPPO)_4 \cdot 2CH_3NO_2$ are given in Table 1. The two nitromethane molecules could be removed by heating under vacuum in a drying pistol or by recrystallization of the complex from acetonitrile.

μ-oxo-hexa-μ-bromotetrakis{ammine copper(II)}, $Cu_4OBr_6(NH_3)_4$

Method One. In an attempt to recrystallize the bromide salt of the copper(II) complex of N(t-butyl)aminoethanol, $Cu(O\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}tbu)Br$, from nitromethane, it was noticed that the solution became very gelatinous as it was heated almost to boiling. This solution was filtered and the filtrate was allowed to stand for several days, after which well-formed red-brown octahedral-shaped crystals were deposited. These crystals were filtered and then dried in a vacuum dessicator. Only a very small amount of this material was formed by this method, but a structure determination confirmed the formula to be $Cu_4OBr_6(NH_3)_4$.

Method Two. The same material in small quantities could be obtained by heating $Cu(O\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}tbu)Br$ in 3-nitropropane. This material was filtered and then dried in a vacuum dessicator. Analytical data for $Cu_4OBr_6(NH_3)_4$ prepared by this method are given in Table 1.

Method Three. Small quantities of $Cu_4OBr_6(NH_3)_4$ could be prepared by heating the bromide salt of the copper(II) complex of 2-phenyl-2-diethylamino ethanol in nitromethane. This material was identified as being the same as the material prepared by method one and method two by unit cell and space group determinations.

μ_4-oxo-hexa-μ-acetatotetrakis copper(II), $Cu_4O(Ac)_6$

Stoichiometric amounts of copper(II) acetate dihydrate and CuO were refluxed in methanol for several hours. Blue-green crystals were deposited on the walls of the flask during this period. The crystals were filtered, and dried in a dessicator. Analytical data for $Cu_4O(AC)_6$ are given in Table 1.

Tetramethylammonium Salt of μ_4-oxo-hexa-μ-chlorotetra{chlorocadiumate(II) , $[(CH_3)_4]_4Cd_4OCl_{10}$

Tetramethylammonium chloride(0.01 mole) and KOH(0.003 mole) were dissolved in a small amount of methanol and $CdCl_2$(0.013 mole) was then added. This solution was heated and filtered while hot. Upon standing, a white crystalline material was precipitated. The crystals were filtered and dried in a vacuum dessicator over sulfuric acid. Analytical data for $[(CH_3)_4]_4Cd_4OCl_{10}$ are summarized in Table 1.

Copper(II) Complex of the Dianion of the 1:1 Schiff's Base of Acetylacetone and 2-aminoethanol, Cu(EIA)

The preparation of this compound was similar to that of Jager (19). Equimolar amounts of 2,4-pentanedione, 2-aminoethanol, and KOH were dissolved in methanol and a methanol solution containing an equivalent amount of copper(II) acetate dihydrate was added. The hot solution was heated and filtered; blue-green crystals separated upon standing. The crystals were filtered and then dried in a vacuum dessicator. Analytical data for Cu(EIA) are given in Table 1.

Copper(II) Complex of the Dianion of the 1:1 Schiff's Base of Acetylacetone and 3-amino-1-propanol, Cu(PIA) (20)

The preparation of Cu(PIA) was the same as that of Cu(EIA) except 3-amino-1-propanol was substituted for 2-aminoethanol. The red-violet

crystalline product was filtered and then dried in a vacuum dessicator. Analytical data for Cu(PIA) are given in Table 1.

Copper(II) Complex of the Dianion of the Schiff's Base of 2-hydroxy-3-methoxybenzaldehyde, Cu(mSALPA)

This complex was prepared by a method similar to that of Cu(PIA) except 2-hydroxy-3-methoxybenzaldehyde was substituted for 2,4-pentanedione. The red-violet crystalline product was filtered and dried in a vacuum dessicator. Analytical data for Cu(mSALPA) are given in Table 1.

Copper(II) Chloride Complex of the Monoanion of the Schiff's Base of Salicylaldehyde and 3-amino-1-propanol, Cu(SALPA)Cℓ

The preparation of Breece (21) was used in preparing this compound. Equimolar amounts of salicylaldehyde and 3-amino-1-propanol were mixed in methanol. One-half of this amount of anhydrous $CuCℓ_2$ was dissolved in methanol and was slowly added to the first solution. The golden-brown crystalline product was filtered and dried in a vacuum. Analytical data for Cu(SALPA)Cℓ are given in Table 1.

Bis{tris(2-aminoethoxido)cobalt(III)}Cobalt(II) diacetate, "Cobalt Trimer"

In an attempt to prepare the cobalt(II) analog of Cu(EIA), this compound was prepared. Equimolar amounts of 2,4-pentanedione, 2-aminoethanol, and KOH were mixed in methanol. An equivalent amount of cobalt(II) acetate tetrahydrate was dissolved in methanol and the two solutions were mixed while hot. The hot solution was filtered and after about one day deep-red octahedral-shaped crystals formed. The crystals were filtered and air dried. Analytical data for the "cobalt trimer" are given in Table 1.

Crystallographic Data and Location of Atomic Positions

Unit Cell Determination

Experimental Methods. A crystal, which appeared to be a single crystal when viewed under a stereoscopic or a polarizing microscope, was chosen for mounting. The crystal was mounted on a thin glass fiber which had been glued to a metal pin. The metal pin was secured into the goniometer head and a coarse adjustment of the arcs by visual examination of the crystal was performed. Final orientation of the crystal was carried out on a Buerger precession camera using unfiltered molybdenum radiation (22).

Unit cell dimensions, diffraction symmetry and other data necessary to define the unit cell and space group were obtained from zero level and upper level photographs using zirconium-filtered molybdenum radiation.

Collection of Intensity Data on Film

After the unit cell and space group data were collected, the collection of intensity data began. Three timed exposures, usually of .50, 5.0, and 0.5 hours, were made; Ilford Industrial-G X-ray film was used. The orientation of the crystal was checked periodically during the collection of the data. The three timed exposures were all carried through the development process simultaneously. The intensities of the reflections were estimated by a visual comparison of the reflection to a standard series.

Collection of Diffractometer Data

When the data were to be collected by counter methods, the crystal and goniometer head were moved from the precession camera to a Picker Four-circle Automated Diffractometer after the preliminary studies. Since the alignment on the diffractometer was more critical than on the precession camera, the crystal was realigned according to published instructions (23). The four angles, ϕ, χ, ω and 2θ, which define the position of the crystal and counter to record a reflection in reciprocal space, were determined for several reflections. From this data, refined unit cell parameters and angle settings for the remaining reflections were obtained by a least-squares method using a computer program (24). The intensities were measured with the scintillation counter mounted 21 centimeters from the crystal. The intensities were collected by the θ - 2θ scan technique with a takeoff angle of 1.6° and a scan rate of 1° per minute. When the scan was completed, stationary background counts were recorded on each side of the scan. Calibrated copper attenuators were used in the collection of the data. The attenuators were calibrated by collecting intensities on thirty different reflections of various magnitudes. The threshold point was set so that attenuators would be inserted automatically when the counting rate exceeded 10,000 counts/second. The pulse height analyzer was set for approximately a 90 per cent window, centered on the molybdenum Kα peak. Corrected intensities (CI) were obtained by the equation

$$CI = CT - S(bgd1 + bdg2)$$

where CT is the total integrated peak count and S is the ratio of the scan time to the total time for counting backgrounds. Weights, W_i, were assigned to each reflection in the refinement process by the formula

$$W_i = 4(CI)/\sigma(I)^2$$

The corrected intensities were assigned standard deviations according to the formula (25)

$$\sigma(I) = [CT + 0.25(tc/tb)^2(bdg1+bdg2) + (PI)^2]^{1/2}$$

where $\sigma(I)$ is the standard deviation for the ith reflection, tc is the total scan time, tb is the counting time of each background, and P is an "ignorance factor" that must be added to keep the very strong reflections from having unreasonably high weights.

Periodic scans of standard reflections were made to check for decomposition, loss of alignments and changes in the electrical circuitry. If any significant changes in the intensities of the standard reflections were noted, the crystal was realigned and the collection of the data was resumed.

Calculations

Computations were carried out on a Burroughs 5500 computer and on the Univac 1108 computer. Programs used include modified versions of F. L. Carter's program for calculating diffractometer settings (24),

Zalkin's FORDAP Fourier summation program (26), Busing, Martin and Levy's ORFLS (27), XFLS (28), and ORFFE (29), a program for calculating Lorentz-polarization corrections by Bertrand (30) a data reduction program by Kirkwood (31), and a program for calculating the best least-squares plane for a set of atoms (see Appendix 1). In all of the structure factor calculations the scattering factors for neutral atoms by Ibers (32) were employed for all atoms.

Determination of Structures

Solution of the Structure of the Tetramethylammonium Salt of $Cu_4OCl_{10}^{-4}$ (18)

An octahedral-shaped crystal with an average trigonal-face to trigonal-face distance of about 0.3 millimeters was chosen for the unit cell determination. Precession photographs, using zirconium-filtered molybdenum Kα(λ = 0.7107Å) radiation, indicated that the crystal was cubic with a unit cell dimension a of 19.30 ± 0.02Å. The calculated density of 1.70 g/cm^3 agreed well with the experimental value of 1.69 ± 0.02 g/cm^3 obtained by the floatation method in a mixture of carbon tetrachloride and methylene iodide. From the density of the crystal and the volume of the unit cell, it was calculated that there were eight formula units of $C_{16}H_{48}N_4Cu_4OCl_{10}$ per unit cell. The Laue symmetry was m3m and the hhl reflections were systematically absent for l odd. Although space groups Pm3m and $P\bar{4}3n$ were possible, only the latter was consistent with the presence of eight anions per unit cell. Successful refinement confirmed $P\bar{4}3n$ as the correct space group.

The same crystal was used to collect intensity data on film. A Buerger precession camera was used to collect a total of 310 unique, non-zero reflections (which were visually estimated as previously described) from the *hkl* (l=0-4) layers. Lorentz-polarization corrections (30) were then computed and applied to the data. The minimum structure factor, Fmin, was obtained by multiplying the least intense spot on the standard series, Imin, by the Lorentz-polarization factor for the reflections and then taking the square root of the product. Since the calculated absorption coefficient, μ, was only $32cm^{-1}$, no corrections were made for absorption (32).

From a three-dimensional Patterson synthesis (33), coordinates were assigned to all atoms except those of the tetramethylammonium ions. The interpretation of the Patterson map was simplified since it was suspected that the basic structural unit would be similar to that found for the other $Cu_4OCl_6L_4$ (10) structure. The eight oxygen atoms occupied a 2a set (site symmetry, 23) and a 6c set (site, symmetry, $\bar{4}$) (34). The copper atoms coordinated to the oxygens atoms of the 2a set (origin anion) occupied an 8e set and the copper atoms coordinated to the oxygen atoms of the 6c set occupied the 24i positions. The bridging chlorides of the origin anion were placed in a 12f set and the bridging chloride of the non-origin anion were placed in 12g and 24i sets. (Since the bridging chlorides occupy equatorial positions in the coordination sphere of the copper, they will be designated Cl_{eq}; primed symbols will be used for the non-origin anion). The terminal chlorides (designated Cl_{ax}) were placed in an 8e set for

the origin anion and in a 24i set for the non-origin anion.

After two cycles of full-matrix least-squares refinement (27) of the coordinates of all of the atoms, the conventional R factor was 0.17 ($R = \Sigma\left|\,|Fo| - |Fc|\,\right|/\Sigma\,|Fo|$). A Fourier synthesis was then computed using the phases calculated for the known part of the structure. From the resulting electron density map, all of the remaining non-hydrogen atoms were located. Least-squares refinement of all atomic coordinates not defined by symmetry, individual isotropic temperature factors, and individual scale factors for the five layers of data was continued until successive cycles gave no appreciable change in any parameter. The final conventional R value was 0.090. Structure factors were then calculated for unobserved reflections and none of the calculated values exceeded two times Fmin. Final structural parameters are listed in Table 2 and observed and calculated structure factors are listed in Table 3.

Solution of the Structure of $Cu_4OBr_6(NH_3)_4$

Crystals of $Cu_4OBr_6(NH_3)_4$, suitable for X-ray diffraction studies, were obtained from method one of the preparation. A well-formed octahedral-shaped crystal with a radius of approximately 0.15 mm was mounted on an apex of the octahedron. Precession camera photographs indicated that the crystal system was tetragonal since $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$. The space group was uniquely defined as being $P\bar{4}2_1c$ since the odd index reflections in the hhl layer and along the $h00$ lines (l = 2n+1 on hhl and h = 2n+1 on $h00$) were systematically absent.

Table 2. Positional and Thermal Parameters for $[(CH_3)_4N]_4[Cu_4OCl_{10}]$

Atom	x	y	z	B(A^2)
O	0.0000	0.0000	0.0000	2.4(2.3)[a]
O'	0.2500	0.5000	0.0000	8.7(3.0)
Cu	0.0582(5)	0.0582	0.0582	4.3(3)
Cu'	0.1922(5)	0.5501(4)	0.0637(4)	3.6(2)
Cl_{eq}	0.1537(20)	0.0000	0.0000	7.2(8)
Cl_{eq},(1)	0.0980(14)	0.5000	0.0000	4.8(5)
Cl_{eq},(2)	0.2457(8)	0.6511(8)	0.0178(8)	3.7(3)
Cl_{ax}	0.1231(13)	0.1231	0.1231	8.2(1.4)
Cl_{ax},	0.1295(9)	0.6100(9)	0.1417(10)	5.5(5)
N	0.3401(34)	0.3401	0.3401	5.1(2.4)
N'	0.8549(39)	0.9243(42)	0.3459(40)	7.3(1.9)
C(1)	0.2955(60)	0.2955	0.2955	12.9(5.9)
C(2)	0.3365(68)	0.4060(49)	0.3251(61)	9.9(3.2)
C'(1)	0.8046(48)	0.9532(47)	0.2916(48)	9.1(2.3)
C'(2)	0.8490(41)	0.8449(41)	0.3276(40)	7.1(1.8)
C'(3)	0.9284(43)	0.9246(43)	0.3371(50)	8.3(2.0)
C'(4)	0.8418(41)	0.9242(36)	0.4108(40)	5.3(1.5)

[a]Numbers in parentheses are the estimated standard deviations occurring in the last digits listed.

Table 3. Observed and Calculated Structure Factors for $[(CH_3)_4N]_4Cu_4OCl_{10}$

H	K	FO	FC
	L=0		
3	3	733	731
4	0	3493	3175
4	2	550	595
4	3	423	463
4	4	4950	4724
6	0	2422	2244
6	1	1719	1779
6	5	828	981
7	3	462	480
7	6	3105	3131
8	0	1967	1511
8	2	1121	1085
8	4	1516	1598
8	6	2298	2434
8	8	6932	7013
9	2	1984	1970
9	4	601	530
9	6	1856	1962
10	0	2582	2687
10	1	2184	2126
10	3	1527	1443
10	5	1270	1394
10	7	1459	1516
10	8	1623	1716
10	9	1168	1235
11	2	1293	1270
11	6	1053	992
11	7	674	724
11	10	703	753
12	4	1172	780
12	5	340	400
12	6	1537	1413
12	7	347	181
12	8	1403	1338
12	10	359	352
12	12	1383	1519
13	2	775	774
13	3	491	526
13	4	349	557
13	5	496	557
13	6	1224	1052
13	12	375	517
14	0	1423	1479
14	1	1744	1595
14	4	507	200
14	5	882	831
15	1	365	409
15	2	517	466
15	3	732	844
15	10	536	539
15	15	551	559
16	0	2237	2381
16	2	1180	1133
16	5	531	439
16	6	376	287
16	8	1316	1234
16	10	542	493
16	11	385	311
16	12	774	690
16	16	669	492
17	2	536	601
17	4	380	460
17	6	540	471
17	10	669	730
17	16	380	168
18	1	941	1022
18	3	544	640
18	7	386	388
18	8	547	551
18	9	671	647
19	2	548	556
20	0	1739	1367
20	2	777	677
20	4	673	468
24	0	625	447
	L=1		
3	2	1239	1050
4	3	2124	2137
4	1	2233	2098
4	2	2172	2004
5	2	570	487
6	2	626	584
6	1	601	656
6	4	1502	1647
6	5	2441	2413
7	2	720	764
7	3	421	592
7	4	303	310
7	5	1158	1102
7	6	2242	2385
8	2	1405	1519
8	4	1017	941
8	5	1601	1535
8	6	2355	2408
8	7	1075	1223
9	2	1761	1867
9	4	830	840
9	5	767	770
9	6	1707	1647
9	8	1021	782
10	1	1395	1235
10	3	2228	2089
10	4	502	614
10	7	2179	2336
10	8	1296	1249
10	9	1076	1260
11	2	1157	1031
11	4	1171	975
11	5	1181	1181
11	6	1306	1274
11	10	398	360
12	1	537	500
12	2	538	546
12	5	948	807
12	6	1460	1374
12	7	557	480
12	11	585	827
13	2	394	332
13	3	791	782
13	4	889	922
13	5	399	418
13	6	697	736
13	10	418	382
14	1	704	636
14	2	575	579
14	3	1527	1274
14	4	409	357
14	6	413	325
14	11	431	484
14	12	616	703
14	13	440	583
15	2	1025	916
15	3	419	421
15	10	615	672
15	11	438	495
15	12	442	297
15	13	445	534
16	1	741	810
16	2	428	591
16	3	607	536
16	5	431	289
16	6	612	560
16	10	765	867
16	13	450	443
17	2	757	784
17	3	619	609
17	6	623	461
17	10	775	844
18	1	1406	1470
18	4	446	289
18	5	446	393
18	6	447	338
18	7	634	379
18	8	636	633
18	9	780	629
18	11	453	453
19	2	637	545
20	2	643	547
22	4	455	294
	L=2		
3	3	1805	1812
4	1	1994	2004
4	2	2267	2325
4	3	2588	2872
4	4	1621	1745
5	1	555	487
5	3	807	821
5	4	2529	2561
5	5	1189	1191
6	1	582	584
6	2	1454	988
6	4	1785	1901
6	6	5256	4925
7	3	1031	990
7	4	1363	1244
7	5	1083	1041
7	7	2565	2506
8	3	1696	1817
8	4	460	665
8	5	1151	1069
8	6	339	410
8	7	1702	1635
8	8	1884	1861
9	3	1672	1769
9	4	977	1054
9	6	356	390
9	7	1360	1325
9	8	1173	1246
9	9	1515	1623
10	2	2264	2557
10	4	728	960
10	5	521	643
10	6	2362	2326
10	10	565	730
11	3	1311	1321
11	4	1525	1429
11	6	550	449
11	7	788	816
11	8	692	741
11	11	592	556
12	3	1478	1428
12	5	693	717
12	6	700	782
12	7	913	1011
12	8	584	614
12	9	418	489
12	12	436	575
13	3	410	269
13	4	922	895
13	5	1245	1161

Table 3. (Continued)

H	K	FO	FC
13	8	425	358
13	12	631	782
13	13	639	748
14	2	2395	2376
14	4	953	893
14	6	862	759
14	8	437	315
14	10	445	659
14	12	455	581
14	14	806	833
15	8	448	453
15	9	639	592
15	12	655	554
16	5	639	687
16	6	454	302
16	7	456	560
16	8	794	791
16	9	799	853
16	11	810	702
17	7	658	668
17	8	661	694
17	9	664	602
18	1	468	323
19	3	477	446

L=3

H	K	FO	FC
5	4	1865	1777
6	3	1879	1844
6	4	1996	1968
7	4	2193	2174
7	6	1421	1527
10	8	435	582
11	4	1135	1180
11	5	434	280
11	6	439	478
11	8	784	664
11	9	651	644
10	6	420	564
9	5	874	872
9	8	723	685
9	7	816	788
10	3	1138	1033
10	4	1995	2021
10	5	584	648
9	6	1056	946
9	4	542	598
8	4	506	559
8	6	1068	1010
8	7	549	704
12	3	1180	1097
12	5	2028	2159
12	6	794	825
12	7	927	823

H	K	FO	FC
12	11	850	1087
13	4	1623	1385
13	6	476	380
13	7	480	430
13	12	722	645
14	4	1086	1081
14	7	496	255
14	11	730	699
14	12	522	551
15	4	710	735
15	12	754	752
16	3	515	534
16	10	927	933
20	3	795	791

L=4

H	K	FO	FC
5	5	2941	3275
6	6	1574	1917
7	5	1819	1673
7	6	1468	1493
7	7	603	524
8	4	1523	1357
8	6	437	388
9	5	785	603
9	6	465	529
9	7	478	533

H	K	FO	FC
10	4	1161	1190
10	5	1366	1364
10	6	697	697
11	5	1251	1413
11	6	734	744
11	7	1180	1134
11	11	569	653
12	4	2124	1943
12	8	969	939
13	5	1374	1413
13	6	1267	1237
13	7	573	698
13	11	604	740
13	13	622	678
14	5	1167	1097
14	6	832	1142
14	7	840	973
14	13	637	771
14	14	645	641
15	5	1209	1169
15	6	608	847
15	11	637	794
16	4	1076	935
16	6	627	357
16	8	899	840
17	6	645	357
19	7	677	638

All of the photographs also showed mirror-mirror (mm) symmetry consistent with the tetragonal classification. The calculated density, 3.44 g/cm^3, based upon two formula units of $Cu_4OBr_6(NH_3)_4$ per unit cell agreed well with the experimental value of 3.35 ± 0.10 obtained by the flotation method in a mixture of iodoform and methylene iodide.

After the space group determination and preliminary alignment was completed, the crystal and goniometer head were moved to the Picker Four-circle Diffractometer and realigned as described earlier (23). The refined unit cell constants obtained by the least-squares method (24) described earlier were $a = b = 9.004(5)$ and $c = 9.731(6)$, where the numbers in parentheses represent the standard deviation in the last figure. A total of 483 unique reflections were collected using a ten second background and a 2° scan. The reflections collected were within the region between 0-8 in h and k and 0-10 in ℓ. No significant changes in the intensities of the standard reflections were noticed during the collection of the data. Of the 483 reflections collected, 340 were accepted as being statistically above background on the basis that $\sigma(I)/CI$ was less than 0.30 with P = 0.02. Since the linear absorption coefficient, μ, was 218 cm^{-1}, it was necessary to correct for absorption (32). Absorption corrections based on a spherical crystal, assuming the octahedral crystal approximated a sphere of radius 0.15 mm were calculated and a corrected set of intensities obtained. Lorentz-polarization corrections (30) were also calculated for the data set. Corrections for the real and imaginary parts of the anomalous dispersion (32) were applied to the bromine and copper atoms. The

coordinates of all of the atoms except the ammonias were found from a three-dimensional Patterson synthesis (33). The Patterson map was quite confusing at first since the exact formula of the compound was not known and this structure was not expected. However, having worked with other μ_4-oxo type structures, the interpretation was straightforward once the nature of the compound was recognized. The oxygen atoms were placed in a 2a set (site symmetry, $\bar{4}$), the copper atoms in the 8e set, and the bromine atoms in 4c and 8e sets. Three cycles of full-matrix least-squares refinement (28) resulted in a conventional R value of 0.15. From an electron density map (26) phased on these atoms, the nitrogen atom was located and placed in the 8e set. After two more cycles of least-squares refinement varying the scale factor, individual atomic coordinates not defined by symmetry, and individual isotropic temperature factors and with all of the data weighted at unity, the conventional R value dropped to 0.13. After further refinement with anisotropic temperature factors and a weighting scheme (25) based on counting statistics ($w_i = 4(CI)/\sigma(I)^2$) values of 0.108 and 0.088 were obtained for R_1 and R_2, where R_1 is the previously defined contentional R factor and

$$R_2 = \{\Sigma_i w_i(|F_o|-|F_c|)^2/\Sigma_i w_i(|F_o|)^2\}^{1/2}.$$

A final difference Fourier showed some intensity in the regions of the hydrogen atoms but these positions were not included in the refinement.

were not included in the refinement. These peaks were in the range of 0.9 to 1.1 electrons in height, thus the proposed structural formula was definitely established since if any heavier atoms had been bonded to the nitrogen, the peaks in the difference Fourier would have been much more intense. The positional parameters derived from the last cycle are presented in Table 4. The anisotropic temperature factors for the atoms are given in Table 5 and the final observed and calculated structure factors are given in Table 6.

Table 4. Final Positional Parameters for $Cu_4OBr_6(NH_3)_4$

Atom	x	y	z
Ocnt	0	0	0
Cu	0.0663(6)	0.1596(5)	0.1147(5)
N	0.1343(36)	0.3245(40)	0.2339(35)
Br8fs	0.3230(5)	0.1281(5)	0.0031(7)
Br4fs	0	0	0.3138(5)

Table 5. Final Anisotropic Thermal Parameters ($X10^4$) for $Cu_4OBr_6(NH_3)_4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ocnt	59(15)	59(15)	50(13)	0	0	0
Cu	68(7)	36(7)	66(4)	- 9(5)	-19(6)	- 5(5)
N	29(12)	55(14)	114(23)	-34(13)	- 2(5)	-35(14)
Br8FS	51(5)	81(6)	102(4)	- 8(4)	8(6)	-25(5)
Br4FS	144(12)	65(10)	60(5)	- 1(11)	0	0

Table 6. Observed and Calculated Structure Factors for $Cu_4OBr_6(NH_3)_4$

H	K	FO	FC
	L= 0		
2	2	96	76
1	3	215	173
2	3	112	93
3	3	135	115
0	4	120	102
1	4	178	153
2	4	138	120
3	4	121	108
4	4	143	130
1	5	65	60
3	5	117	109
4	5	65	60
5	5	101	101
0	6	180	176
1	6	74	70
2	6	123	113
4	6	31	13
5	6	28	30
1	7	52	41
2	7	26	13
3	7	148	152
6	7	57	60
0	8	34	3
1	8	47	46
2	8	34	26
3	8	55	58
4	8	83	87
5	8	28	10
6	8	33	28
8	8	35	22
	L= 1		
1	2	122	111
0	3	56	49
1	3	73	66
2	3	63	56
0	4	28	17
1	4	64	57
2	4	191	166
3	4	107	91
0	5	165	144
1	5	88	77
2	5	38	33
4	5	97	95
0	6	83	82
1	6	51	52
2	6	55	49
3	6	25	9
4	6	56	52
5	6	78	76
0	7	25	21
1	7	85	89
2	7	34	39
3	7	30	21
5	7	78	78
0	8	29	20
1	8	84	86
2	8	51	53
3	8	92	90
4	8	35	32
5	8	31	34
7	8	35	42
	L= 2		
1	1	139	142
0	2	112	122
1	2	203	199
2	2	128	125
0	3	114	116
1	3	89	79
2	3	72	64
3	3	169	157
0	4	156	151
1	4	112	102
2	4	36	27
3	4	71	63
4	4	95	91
0	5	54	45
1	5	66	62
2	5	99	95
3	5	65	62
4	5	59	61
5	5	77	82
0	6	37	27
1	6	91	87
2	6	40	38
3	6	43	40
4	6	82	79
6	6	29	25
0	7	78	77
1	7	51	52
2	7	39	32
3	7	42	35
4	7	38	37
5	7	45	48
6	7	51	51
0	8	38	33
1	8	33	35
2	8	46	49
3	8	43	47
4	8	37	39
6	8	30	24
8	8	46	43
	L= 3		
0	1	68	64
0	2	60	66
1	2	91	94
0	3	143	145
1	3	122	128
2	3	169	168
0	4	45	44
1	4	128	128
2	4	30	23
3	4	41	42
0	5	25	22
1	5	48	48
2	5	82	79
3	5	82	83
4	5	117	119
0	6	66	67
1	6	85	79
2	6	94	95
4	6	57	61
5	6	37	35
0	7	85	85
1	7	79	83
2	7	31	25
3	7	54	51
4	7	33	27
5	7	37	35
6	7	75	81
0	8	41	33
2	8	30	25
3	8	80	85
4	8	33	30
5	8	36	40
6	8	38	43
	L= 4		
0	0	65	56
1	1	129	133
0	2	78	78
1	2	118	125
2	2	58	59
0	3	38	35
1	3	141	149
2	3	33	28
3	3	68	71
0	4	62	47
1	4	29	26
2	4	70	75
3	4	26	19
4	4	39	32
0	5	28	17
2	5	143	149
3	5	33	30
4	5	28	22
5	5	57	60
0	6	56	59
2	6	51	52
3	6	35	35
4	6	59	65
6	6	52	60
0	7	29	32
1	7	29	28
2	7	36	38
4	7	50	50
6	7	26	22
7	7	38	40
0	8	35	40
1	8	28	7
2	8	33	28
3	8	29	23
4	8	27	10
5	8	32	33
6	8	41	46
8	8	39	46
	L= 5		
0	1	139	142
0	2	36	36
1	2	89	93
1	3	91	92
2	3	46	39
2	4	25	24
3	4	85	93
0	5	111	118
1	5	43	42
2	5	39	40
3	5	66	71
4	5	30	27
0	6	44	45
1	6	32	32
2	6	70	79
3	6	91	102
4	6	44	46
5	6	39	42
1	7	56	59
2	7	75	82
3	7	46	44
4	7	41	43
6	7	42	46
1	8	43	47
6	8	30	26

Table 6. (Continued)

H	K	FO	FC
	L= 6		
0	0	128	129
0	1	27	26
1	1	26	25
1	2	101	110
2	2	105	113
0	3	60	66
1	3	117	127
2	3	27	21
3	3	27	18
1	4	38	37
2	4	78	77
4	4	82	83
0	5	39	40
1	5	33	37
2	5	80	87
3	5	40	31
4	5	28	33
5	5	83	86
0	6	69	75
1	6	49	55
3	6	28	20
6	6	37	46
0	7	54	61
2	7	31	34
3	7	35	39
4	7	36	28
6	7	28	32
7	7	34	33
0	8	39	35
2	8	28	21
4	8	37	45
6	8	33	36
	L= 7		
0	1	65	63
0	2	58	61
1	2	47	46
0	3	29	26
1	3	50	48
2	3	49	51
1	4	28	28
2	4	61	65
3	4	34	32
0	5	34	32
2	5	37	35
4	5	66	67
0	6	63	67
1	6	38	43
2	6	28	30
4	6	38	42
5	6	27	19
0	7	31	34
1	7	52	51
3	7	30	28
4	7	28	20
5	7	40	42
3	8	55	58
5	8	26	18
	L= 8		
0	0	114	114
0	1	25	20
1	1	45	40
0	2	66	67
1	2	49	47
2	2	66	70
1	3	33	29
2	3	39	36
3	3	114	116
0	4	102	108
1	4	64	62
2	4	37	29
3	4	44	42
4	4	4[illegible]	37
1	5	48	43
3	5	26	20
4	5	33	28
1	6	40	39
4	6	37	38
6	6	36	37
1	7	35	30
4	7	25	11
5	7	37	40
6	7	28	27
7	7	34	34
0	8	41	41
1	8	29	19
2	8	32	25
3	8	35	28
4	8	31	21
7	8	27	8
8	8	34	30
	L= 9		
0	1	84	82
0	2	27	5
1	3	26	14
1	4	25	12
2	4	65	63
0	5	31	25
1	5	37	34
2	5	40	36
4	5	50	45
0	6	26	7
1	6	42	40
3	6	34	24
4	6	27	14
5	6	28	17
0	7	31	25
1	7	31	21
2	7	33	25
3	7	26	7
4	7	28	17
5	7	33	30
1	8	31	21
2	8	28	23
3	8	50	51
4	8	27	18
	L=10		
0	0	112	110
1	1	39	35
1	2	41	37
2	2	30	22
0	3	33	30
1	3	44	39
2	3	28	22
3	3	25	15
1	4	42	36
2	4	37	30
3	4	35	25
4	4	40	38
0	5	29	8
2	5	34	9
3	5	37	32
5	5	39	32
0	6	43	37
1	6	31	27
2	6	36	28
4	6	28	17
0	7	30	26
3	7	42	37
4	7	31	7
5	7	32	7
7	7	27	4
0	8	29	1
1	8	29	18
3	8	29	15
4	8	31	21
5	8	30	3
6	8	30	15
7	8	32	5

Solution of the Structure of Cu(PIA) (20)

Suitable crystals for diffraction work were obtained from the preparation of the compound. A needle-like crystal with approximate dimensions 0.10 x 0.17 x 0.60 mm was mounted along the long dimension and precession photographs were taken. The crystal was found to be monoclinic with a = 5.98(1)Å, b = 10.97(2)Å, c = 14.42(2)Å, and β = 106.75(10)°. The density calculated on the basis of four formula units per unit cell, 1.61 g/cm^3, agreed well with experimental value, 1.61(2) g/cm^3, obtained by the flotation method in a mixture of carbon tetrachloride and methylene iodide. The space group was uniquely defined as $P2_1/c$ since the systematic absence of the reflections with l = 2n+1 on the $h0l$ zone and the systematic absence of the reflections with k = 2n+1 on the $0k0$ line were consistent only with this space group.

Intensity data were collected on the Buerger precession camera using the same crystal as used for the space group determination. A total of 631 unique, non-zero reflections were usually estimated from the $hkl(l = 0\text{-}\bar{3})$ and $hkl(k = 0\text{-}2)$ layers. Lorentz-polarization corrections (30) were made but no corrections for absorption were made since the linear absorption coefficient was small (μ = 24 cm^{-1}).

The coordinates of the copper atom were located from a three dimensional Patterson synthesis (33). After two cycles of full-matrix least-squares refinement (28), the conventional R value was 0.32. From an electron density map (26) phased on the copper atom, the positions of the atoms comprising the coordination sphere of the copper atom were

determined. At this point the conventional R value was 0.24 and another electron density map, phased on the atoms located, revealed the remaining atoms. Four cycles of full-matrix least-squares refinement varying the seven individual scale factors, atomic coordinates and individual isotropic temperature factors converged to a conventional R value of 0.100. At this point there were no significant changes in any parameter. The final structural parameters are listed in Table 7 and observed and calculated structure factors are listed in Table 8.

Table 7. Final Positional and Thermal Parameters for Cu(PIA)

Atom	x	y	z	B, A^2
Cu1	0.1068(4)	0.0322(2)	0.1055(2)	4.02(6)
O2	-0.1465(21)	0.0659(13)	-0.0015(9)	4.89(30)
C3	-0.3369(33)	0.1486(21)	-0.0102(15)	5.04(44)
C4	-0.1792(38)	0.2189(26)	0.1710(18)	6.20(52)
N5	0.0297(25)	0.1377(17)	0.2013(12)	4.57(34)
C6	0.1506(34)	0.1398(22)	0.2908(16)	4.96(44)
C7	0.0719(37)	0.2174(25)	0.3636(17)	6.31(54)
C8	0.3489(31)	0.0695(20)	0.3327(14)	4.66(41)
C9	0.4662(34)	-0.0068(24)	0.2819(15)	5.67(47)
C10	0.6916(35)	-0.0719(22)	0.3353(16)	5.79(49)
O11	0.3762(22)	-0.0275(15)	0.1892(10)	5.59(31)
C12	-0.2506(40)	0.2544(25)	0.0637(20)	8.07(65)

Table 8. Observed and Calculated Structure Factors for Cu(PIA)

H	K	FO	FC
	L=0		
0	4	693	683
0	6	210	150
0	0	224	198
0	2	133	114
1	3	587	535
1	4	197	176
1	5	216	191
1	6	56	67
1	7	252	250
1	9	152	133
1	0	118	115
1	1	98	81
1	2	125	122
2	2	238	270
2	3	233	286
2	5	203	225
2	6	191	199
2	7	428	446
2	8	88	66
2	9	429	408
2	1	186	170
3	2	163	185
3	3	125	126
3	4	240	244
3	5	267	287
3	7	215	221
3	9	229	200
3	1	79	93
4	2	423	452
4	3	117	137
4	4	187	207
4	5	219	230
4	6	61	67
4	7	95	100
4	8	68	56
4	9	37	40
4	0	82	67
5	2	227	254
5	4	135	154
5	5	68	41
5	6	44	48
6	4	103	99
6	5	89	88
	L=-1		
-6	4	103	91
-6	6	110	113
-5	3	92	106
-5	4	84	91
-5	5	71	82
-5	6	121	135
-5	8	95	87
-5	0	67	68
-4	3	281	263
-4	5	145	176
-4	1	87	74
-3	3	440	496
-3	5	253	208
-3	6	82	67
-3	7	65	85
-3	8	119	119
-3	9	58	49
-3	0	38	50
-3	1	67	73
-3	2	39	31
-3	3	55	47
-2	2	510	404
-2	3	70	45
-2	4	381	388
-2	5	76	70
-2	6	289	288
-2	7	45	53
-2	8	384	364
-2	9	43	23
-2	0	156	176
-2	1	54	63
-2	2	55	63
-1	3	234	223
-1	4	278	297
-1	5	44	46
-1	6	412	443
-1	7	115	151
-1	8	529	428
-1	9	41	36
-1	0	339	314
-1	2	116	110
0	3	545	540
0	5	214	264
0	6	156	204
0	7	91	106
0	8	184	185
0	9	115	114
0	0	163	163
0	1	117	118
0	3	79	73
1	3	971	887
1	6	90	108
1	7	83	107
1	8	77	69
1	9	101	116
1	0	50	56
1	1	118	124
1	2	47	46
1	3	97	87
2	5	39	62
2	6	249	276
2	7	104	99
2	8	257	278
2	9	49	64
2	0	121	129
2	1	100	97
2	2	67	68
3	2	161	211
3	4	276	340
3	5	151	158
3	6	368	358
3	7	144	180
3	8	274	279
3	0	171	166
3	2	68	75
4	2	121	141
4	3	228	256
4	4	218	253
4	5	60	68
4	6	226	244
4	7	36	35
4	8	154	147
4	0	95	97
5	2	90	106
5	3	153	209
5	4	99	123
5	6	76	97
5	8	72	78
6	1	123	134
6	3	145	158
6	5	87	79
	L=-2		
-7	0	70	89
-7	2	106	91
-6	2	126	76
-5	0	37	46
-5	3	101	102
-5	5	181	172
-5	7	162	134
-5	9	105	98
-5	1	56	63
-4	2	290	254
-4	3	92	103
-4	5	113	141
-4	6	73	73
-4	7	166	149
-4	9	95	99
-4	1	69	58
-3	2	677	644
-3	4	316	323
-3	5	79	99
-3	6	33	39
-3	7	59	69
-3	0	100	85
-3	2	80	74
-3	4	69	56
-2	2	694	679
-2	3	102	154
-2	4	308	286
-2	6	180	177
-2	7	130	153
-2	9	92	105
-2	0	89	94
-2	1	53	43
-2	2	55	61
-2	4	70	50
-1	3	335	314
-1	4	159	177
-1	5	555	508
-1	6	209	212
-1	7	486	474
-1	9	286	292
-1	0	60	76
-1	1	201	187
-1	2	66	62
0	3	402	350
0	5	559	537
0	7	429	381
0	8	84	103
0	9	322	296
0	1	154	137
0	3	56	52
0	4	57	29
1	3	755	752
1	4	593	666
1	5	325	328
1	6	132	165
1	7	252	277
1	8	105	110
1	9	218	217
1	2	66	58
1	4	81	75
2	2	793	810
2	3	291	367
2	4	248	330
2	5	53	73
2	6	90	89
2	8	90	101
2	9	47	62
2	0	61	81
2	2	102	86
2	4	70	76
3	2	232	274
3	3	63	95
3	4	323	303
3	5	474	430

Table 8. (Continued)

H	K	FO	FC
3	6	266	251
3	7	277	255
3	8	91	102
3	9	143	138
3	0	52	64
3	1	86	86
3	2	68	64
3	4	70	52
4	3	155	177
4	4	82	81
4	5	287	269
4	7	210	228
4	9	120	126
4	1	88	87
5	2	96	110
5	3	260	262
5	4	98	121
5	5	159	194
5	7	163	173
5	9	96	91
5	1	56	31
6	2	111	133
6	4	104	109
6	7	40	53
7	2	99	82
7	4	69	60
7	6	69	43

L=-3

H	K	FO	FC
-7	1	116	81
-6	3	131	95
-5	2	106	94
-5	3	158	112
-5	4	124	109
-5	6	142	105
-5	8	102	90
-5	0	80	64
-4	2	176	140
-4	4	151	123
-4	6	221	166
-4	8	238	187
-4	0	157	127
-3	2	197	175
-3	3	346	296
-3	4	251	241
-3	5	116	123
-3	6	214	178
-3	8	198	168
-3	0	114	91
-3	1	63	49
-3	3	66	50
-2	2	220	173
-2	3	562	562
-2	4	464	448
-2	5	213	189
-2	6	178	138
-2	7	50	41
-2	8	74	78
-2	9	110	98
-2	1	113	88
-2	3	65	68
-1	3	383	389
-1	4	243	238
-1	5	244	237
-1	6	463	392
-1	7	64	72
-1	8	77	60
-1	0	103	93
-1	1	82	88
-1	2	43	37
-1	3	78	61
0	4	574	595
0	5	384	347
0	6	737	645
0	8	392	328
0	0	241	199
0	2	120	112
0	3	89	78
1	4	361	433
1	5	157	163
1	6	437	419
1	7	131	123
1	8	395	346
1	0	179	153
1	2	113	99
1	3	44	36
2	3	601	744
2	4	633	754
2	5	441	525
2	6	436	471
2	8	223	204
2	0	56	62
2	1	41	49
2	2	75	54
2	3	90	78
3	3	343	339
3	5	222	231
3	6	69	35
3	7	96	86
3	8	38	15
3	1	75	76
3	3	80	60
4	2	112	114
4	3	396	391
4	4	309	313
4	5	254	262
4	6	276	268
4	7	69	59
4	8	117	94
4	3	66	53
5	2	107	103
5	3	58	41
5	4	176	158
5	6	200	183
5	8	140	134
5	0	91	74
6	2	77	84
6	4	119	114
6	6	151	136
6	8	80	83
7	3	66	62
7	5	66	46

H	L	FO	FC

K=0

H	L	FO	FC
-7	2	98	106
-7	6	75	81
-7	8	98	101
-6	2	155	180
-6	6	276	334
-6	10	58	68
-5	2	154	178
-5	4	153	175
-5	6	233	260
-5	8	159	180
-5	10	222	223
-5	14	102	104
-4	2	151	137
-4	4	281	291
-4	6	68	64
-4	8	408	408
-4	10	244	279
-4	14	175	179
-3	2	352	428
-3	4	335	394
-3	8	643	635
-3	10	132	138
-3	12	349	342
-3	16	79	77
-2	2	235	220
-2	4	502	491
-2	6	914	852
-2	8	427	410
-2	10	332	307
-2	12	171	132
-2	16	213	170
-1	2	602	651
-1	4	445	416
-1	6	750	732
-1	8	81	84
-1	10	478	497
-1	12	270	202
-1	14	108	99
-1	16	104	93
0	4	626	525
0	10	665	565
1	2	62	70
1	4	799	781
1	6	30	25
1	8	482	512
1	10	175	209
1	12	311	259
1	14	111	120
2	2	655	690
2	4	594	579
2	6	230	255
2	8	406	392
2	12	261	231
2	14	66	38
3	0	195	186
3	2	644	645
3	4	114	137
3	6	317	351
3	10	116	125
3	12	121	116
4	0	473	546
4	2	297	327
4	4	233	229
4	6	49	62
4	10	142	147
5	0	238	280
5	4	195	242
5	6	65	61
5	8	107	101
6	2	65	73
6	4	151	155

K=1

H	L	FO	FC
-7	3	97	103
-7	7	106	126
-7	11	61	55
-7	13	60	49
-6	4	79	65
-6	5	112	118
-6	7	189	211
-6	9	30	44
-6	11	121	134
-6	15	81	83
-5	3	28	37
-5	4	74	84
-5	5	331	380
-5	9	220	224

Table 8. (Continued)

H	L	FO	FC	H	L	FO	FC	H	L	FO	FC	H	L	FO	FC
-5	11	116	123	0	8	116	114	-7	8	107	119	-1	9	223	216
-5	12	41	39	0	9	599	567	-7	12	48	69	-1	10	320	304
-5	15	118	107	0	11	358	308	-6	5	56	85	-1	11	226	213
-4	1	284	297	0	13	196	190	-6	6	171	194	-1	12	189	195
-4	2	67	74	0	15	66	81	-6	10	122	118	-1	13	97	107
-4	3	279	311	0	16	61	39	-6	12	81	72	-1	14	177	142
-4	5	277	239	1	2	268	209	-6	14	67	45	-1	16	111	96
-4	6	88	95	1	3	642	661	-6	16	68	66	0	5	132	117
-4	7	153	173	1	4	306	273	-5	4	232	267	0	6	268	238
-4	8	44	45	1	5	384	361	-5	5	133	159	0	7	252	223
-4	9	407	380	1	7	259	238	-5	6	157	155	0	8	306	258
-4	11	67	70	1	9	464	472	-5	7	126	128	0	9	147	150
-4	12	56	47	1	11	84	82	-5	8	30	43	0	10	463	442
-4	13	192	185	1	12	27	26	-5	10	193	191	0	11	155	143
-4	15	42	58	1	13	141	157	-5	11	87	98	0	14	192	173
-4	17	82	68	1	15	52	57	-5	12	54	47	0	16	56	45
-3	1	300	317	1	16	53	35	-5	14	112	116	0	17	58	45
-3	3	379	423	2	0	268	269	-5	16	58	59	0	18	83	67
-3	4	87	110	2	1	188	207	-4	4	355	394	1	4	444	457
-3	5	197	195	2	2	96	98	-4	7	240	245	1	5	520	517
-3	6	158	206	2	3	880	878	-4	8	271	253	1	6	186	172
-3	7	604	599	2	4	106	136	-4	10	154	172	1	7	188	224
-3	8	66	92	2	5	55	70	-4	11	76	63	1	8	479	477
-3	9	264	260	2	6	75	57	-4	12	51	42	1	10	223	220
-3	11	150	154	2	7	442	472	-4	14	164	145	1	11	88	114
-3	13	195	151	2	10	110	117	-4	17	75	60	1	12	117	125
-3	17	151	135	2	11	120	148	-4	18	83	75	1	14	118	115
-2	1	463	465	2	13	127	115	-3	4	156	185	1	15	56	35
-2	2	164	113	3	0	228	280	-3	5	200	220	1	16	33	32
-2	3	477	486	3	1	737	804	-3	6	144	166	1	18	68	53
-2	5	219	223	3	2	53	73	-3	7	115	121	1	18	68	53
-2	6	324	255	3	3	290	341	-3	8	541	564	2	6	205	230
-2	7	812	763	3	4	133	166	-3	9	100	117	2	8	240	241
-2	8	190	210	3	5	284	321	-3	10	51	67	2	10	65	49
-2	9	67	92	3	7	77	110	-3	11	113	109	2	11	120	103
-2	10	66	71	3	9	64	48	-3	12	329	298	2	12	132	152
-2	11	443	369	3	11	211	186	-3	15	53	50	2	14	32	49
-2	12	183	155	3	13	61	60	-3	16	85	74	2	15	67	45
-2	13	54	67	3	15	74	67	-3	18	75	66	2	16	68	53
-2	15	101	107	4	0	105	142	-2	1	127	85	3	4	91	95
-2	17	123	111	4	3	77	88	-2	3	337	311	3	5	115	146
-1	4	274	226	4	4	112	137	-2	4	294	310	3	6	332	393
-1	5	506	497	4	5	180	227	-2	5	230	214	3	9	81	67
-1	6	247	200	4	6	81	102	-2	6	727	737	3	10	154	156
-1	7	329	324	4	7	77	75	-2	8	390	368	3	12	113	92
-1	8	171	123	4	9	124	130	-2	9	97	91	3	13	47	47
-1	9	309	267	4	11	86	103	-2	10	287	263	4	4	133	151
-1	10	80	58	5	1	109	133	-2	11	51	46	4	6	152	178
-1	11	466	414	5	5	148	174	-2	12	207	204	4	9	46	55
-1	12	216	166	5	9	86	101	-2	13	74	87	4	10	141	136
-1	15	207	166	6	5	61	73	-2	15	81	80	5	4	112	134
0	3	168	115					-2	16	156	132	5	5	93	95
0	4	111	99		K=2			-1	5	538	541	5	6	94	83
0	5	516	521					-1	6	701	648	5	7	67	62
0	7	78	50	-7	6	48	65	-1	8	125	139	5	8	82	86

Solution of the Structure of Cu(EIA) (20)

Suitable crystals for single-crystal X-ray work were obtained directly from the preparation of the compound. A needle-like crystal with approximate dimensions 0.10 x 0.15 x 0.60 mm was mounted along the long dimension and precession photographs were taken. The crystal was found to be tetragonal with $a = b = 14.46(2)\text{Å}$, and $c = 7.63(2)\text{Å}$. The density calculated on the basis of eight formula units per unit cell, 1.71 g/cm^3, agreed well with the experimental value of 1.70(2) g/cm^3, obtained by the flotation method in a mixture of carbon tetrachloride and methylene iodide. The systematic absence of hhl reflections with l = 2n+1 and the systematic absence of $h00$ reflections with h = 2n+1 were consistent only with the space group $P\bar{4}2_1c$.

Intensity data were collected with the Buerger precession camera (22). A total of 344 unique, non-zero reflections were estimated visually for the $hkl(k = 0\text{-}4)$ and hhl layers. Lorentz-polarization corrections (30) were made but no corrections were made for absorption (μ = 31 cm^{-1}).

The coordinates of the copper atom were found from a three-dimensional Patterson synthesis (33). Three cycles of full-matrix least-squares refinement (28) resulted in a conventional R value of 0.28. Successive structure factor calculations and electron density maps (26) revealed the positions of the remaining non-hydrogen atoms. Full-matrix least-squares refinement of all atomic coordinates, individual isotropic temperature factors, and individual layer scale factors was continued until no parameter showed any significant change;

the final conventional R value was 0.089. The final atom coordinates and thermal parameters are listed in Table 9 and the observed and calculated structure factors are listed in Table 10.

Table 9. Final Positional and Thermal Parameters for Cu(EIA)

Atom	x	y	z	B, A^2
Cu1	0.0493(2)	0.0915(2)	0.1619(5)	2.57(6)
O2	0.0797(13)	-0.0418(12)	0.1405(19)	2.29(32)
C3	0.1435(22)	-0.0629(22)	0.2716(35)	3.21(60)
C4	0.2166(22)	0.0114(24)	0.2783(34)	2.93(58)
N5	0.1652(18)	0.1035(18)	0.2758(28)	3.06(44)
C6	0.1994(22)	0.1750(22)	0.3575(35)	3.18(55)
C7	0.2878(23)	0.1767(23)	0.4474(39)	3.93(71)
C8	0.1531(22)	0.2622(21)	0.3442(44)	3.35(56)
C9	0.0710(23)	0.2798(21)	0.2560(36)	3.08(55)
C10	0.0288(28)	0.3774(30)	0.2435(48)	5.21(86)
O11	0.0198(16)	0.2198(15)	0.1735(32)	4.08(47)

Table 10. Observed and Calculated Structure Factors for Cu(EIA)

H	L	FO	FC
	K=0		
6	0	1020	938
8	0	809	822
16	0	312	250
2	1	588	546
3	1	811	797
4	1	585	538
5	1	452	462
6	1	823	846
7	1	773	756
8	1	560	566
10	1	809	902
12	1	469	465
15	1	194	116
16	1	241	168
0	2	2909	2957
1	2	293	320
2	2	951	794
3	2	988	905
5	2	460	475
6	2	434	470
7	2	102	128
8	2	186	148
9	2	666	713
11	2	491	468
13	2	263	272
15	2	195	162
16	2	139	119
17	2	276	268
1	3	1645	1681
3	3	978	901
5	3	652	656
6	3	398	283
7	3	818	934
10	3	122	152
11	3	126	78
12	3	130	104
15	3	239	224
0	4	726	675
2	4	534	484
3	4	853	921
5	4	227	206
6	4	492	434
7	4	237	189
8	4	421	382
9	4	466	470
11	4	453	388
13	4	272	258
14	4	194	161
15	4	137	128
1	5	206	186
2	5	339	376
3	5	208	154
4	5	271	313
7	5	178	204
8	5	222	216
10	5	458	412
12	5	333	362
15	5	134	55
0	6	808	887
2	6	512	507
6	6	453	435
8	6	266	289
9	6	189	112
14	6	185	134
1	7	597	660
2	7	189	172
3	7	189	172
4	7	232	248
5	7	300	258
6	7	190	161
7	7	270	254
10	7	233	253
12	7	261	245
5	8	233	249
9	8	260	273
11	8	210	251
1	9	416	438
3	9	130	80
5	9	128	133
7	9	173	210
0	10	397	372
	K=1		
4	0	837	681
5	0	747	723
6	0	975	898
7	0	1134	1073
8	0	682	670
9	0	412	361
10	0	189	191
11	0	163	71
12	0	343	346
14	0	264	258
15	0	237	197
16	0	140	110
17	0	143	134
3	1	271	268
4	1	508	490
5	1	612	708
6	1	768	702
7	1	413	426
8	1	463	425
9	1	575	601
11	1	691	684
12	1	173	167
13	1	180	136
15	1	238	235
16	1	141	112
17	1	203	196
1	2	1107	1100
2	2	765	651
3	2	803	753
4	2	508	470
5	2	632	599
6	2	667	658
7	2	422	420
8	2	391	381
9	2	190	155
12	2	396	359
16	2	246	262
2	3	1190	1134
3	3	407	450
4	3	220	285
5	3	600	606
6	3	812	933
7	3	434	439
8	3	477	500
9	3	404	406
11	3	125	105
12	3	129	57
13	3	133	133
14	3	137	131
15	3	198	192
16	3	202	173
1	4	761	918
2	4	286	326
3	4	438	456
4	4	471	416
5	4	480	484
6	4	282	287
7	4	501	533
8	4	242	302
10	4	476	520
12	4	299	284
14	4	140	114
16	4	202	204
2	5	340	357
3	5	513	516
4	5	122	145
5	5	246	304
6	5	250	284
9	5	414	424
11	5	333	354
13	5	140	184
15	5	201	145
1	6	686	813
3	6	184	183
5	6	263	296
6	6	188	225
7	6	464	469
8	6	234	249
10	6	195	154
14	6	141	120
2	7	306	353
3	7	275	279
4	7	194	170
5	7	239	233
6	7	277	276
7	7	139	161
8	7	198	166
9	7	243	265
11	7	244	215
13	7	197	152
3	8	200	217
4	8	141	187
5	8	141	155
6	8	141	167
8	8	141	104
10	8	242	276
2	9	200	191
6	9	139	171
7	9	138	135
	K=2		
5	0	690	651
6	0	1336	1244
7	0	1334	1400
9	0	462	442
11	0	173	125
13	0	544	524
15	0	418	412
16	0	265	229
4	1	453	427
5	1	604	595
6	1	602	671
7	1	364	383
8	1	522	526
9	1	192	223
10	1	553	471
11	1	176	170
12	1	226	235
14	1	286	247
15	1	148	140
16	1	217	219
17	1	224	213
3	2	224	225
4	2	820	842
5	2	208	214
6	2	525	503
7	2	557	568
8	2	192	158
9	2	497	477

Table 10. (Continued)

H	L	FO	FC
11	2	446	443
12	2	190	160
13	2	198	211
15	2	261	257
16	2	220	188
17	2	159	130
3	3	172	137
4	3	547	504
5	3	568	582
6	3	591	608
7	3	614	668
8	3	763	856
10	3	225	192
11	3	190	171
12	3	197	203
13	3	144	103
14	3	366	382
15	3	153	125
16	3	273	238
17	3	160	123
2	4	682	789
3	4	202	191
4	4	673	734
5	4	421	425
6	4	658	601
7	4	441	416
8	4	185	224
9	4	465	494
10	4	138	101
11	4	284	308
12	4	206	159
13	4	299	264
15	4	222	180
17	4	161	137
3	5	524	564
4	5	296	247
5	5	501	505
7	5	239	210
8	5	199	189
10	5	292	316
11	5	149	118
12	5	215	206
15	5	159	110
16	5	227	166
2	6	426	371
3	6	202	160
4	6	203	156
5	6	323	347
6	6	462	471
7	6	511	432
8	6	211	210
9	6	302	282
10	6	153	105
13	6	275	248
15	6	227	180
3	7	304	356
4	7	152	148
5	7	307	343
6	7	267	270
7	7	219	198
8	7	270	304
10	7	223	180
12	7	226	158
14	7	159	140
16	7	154	151
2	8	274	263
4	8	275	267
5	8	159	188
11	8	160	167
1	9	229	191
6	9	161	205
8	9	159	181

K=3

H	L	FO	FC
6	0	1298	1290
7	0	658	626
8	0	1108	1069
12	0	290	312
13	0	306	274
14	0	574	545
16	0	412	382
17	0	161	172
6	1	551	491
7	1	607	562
8	1	207	200
9	1	470	446
10	1	333	321
11	1	176	131
12	1	131	119
13	1	338	349
15	1	301	248
16	1	271	221
17	1	162	122
18	1	236	203
6	2	685	629
7	2	232	215
8	2	383	394
9	2	234	244
10	2	246	199
11	2	183	124
12	2	191	183
13	2	141	117
14	2	208	206
15	2	153	90
16	2	275	191
17	2	231	194
4	3	345	365
5	3	445	464
6	3	481	477
7	3	818	872
8	3	171	161
9	3	591	618
10	3	293	334
11	3	193	145
12	3	245	287
13	3	509	506
15	3	415	376
16	3	161	107
3	4	772	782
5	4	568	646
6	4	432	458
8	4	396	454
9	4	136	191
10	4	140	167
11	4	204	170
12	4	210	196
14	4	315	298
16	4	165	183
4	5	597	632
5	5	135	144
6	5	276	243
7	5	281	341
8	5	202	212
9	5	253	261
10	5	149	116
4	6	207	201
5	6	296	312
6	6	335	374
8	6	343	430
9	6	155	165
12	6	230	214
14	6	289	330
16	6	169	157
4	7	352	376
5	7	224	196
6	7	225	195
7	7	321	347
8	7	162	110
9	7	163	207
3	8	286	315
5	8	166	176
7	9	241	219

H	K	FO	FC

L=0

H	K	FO	FC
3	3	420	332
4	4	317	358
5	5	356	347
8	8	182	153
9	9	157	143
10	10	437	489
11	11	512	503
12	12	438	398

L=2

H	K	FO	FC
2	2	853	784
3	3	911	903
4	4	586	591
5	5	480	502
6	6	331	317
7	7	595	572
8	8	374	437
9	9	196	214
10	10	167	196
11	11	241	223
12	12	208	169

L=4

H	K	FO	FC
4	4	470	494
5	5	231	190
6	6	386	319
7	7	565	544
8	8	324	328
9	9	235	213
10	10	207	238
11	11	206	269

L=6

H	K	FO	FC
4	4	196	197
6	6	164	161
7	7	262	324
8	8	118	119
9	9	166	166
10	10	227	277

L=8

H	K	FO	FC
4	4	165	257
5	5	164	192

Solution of the Structure of Cu(SALPA)Cℓ

Suitable crystals for single-crystal work were obtained by the recrystallization of the powdered material from methanol with a few drops of hydrochloric acid added. A needle-like crystal of approximate dimensions 0.10 x 0.12 x 0.50 mm was mounted along the long dimension of the crystal. Precession photographs indicated that the crystal was monoclinic. The systematic absence of the l = 2n+1 reflections in the $h0l$ zone and the systematic absence of the k = 2n+1 reflections along the $0k0$ line uniquely defined the space group as $P2_1/c$. The crystal and goniometer head were then transferred to the diffractometer where final adjustments were made (23). Six reflections were scanned and used as input data for the least-squares program (24). The final unit cell dimensions obtained by the least-squares method are a = 8.564(3), b = 12.353(5), c = 10.305(4) and β = 98.43(3). The calculated density based on four formula units per unit cell, 1.71 g/cm^3, agreed well with the observed value, 1.69(2) g/cm^3, obtained by the flotation method in a mixture of carbon tetrachloride and methylene iodide. The data were collected by methods described earlier. To insure that the low-angle reflections were collected first, the data were collected in four batches depending upon the 2θ values of the reflections. The ranges were 0.00 to 15.00°, 15.01 to 25.00°, 25.01 to 40.00° and above 40.01°. A total of 1256 reflections were collected using a 20-second background count and a 2° scan. The reflections collected were in the region between 0-7 in h, 0-9 in k and -8 to +8 in l. After approximately 20 per cent of the data had been collected, the

intensities of the two standard reflections sharply increased by about 10 per cent. The intensities of the standard reflections had been very constant before this increase, and were also very constant at the new value after the increase. This change was probably due to some electronic changes within the diffractometer circuitry. Because of this change, the data were broken into two parts and each part assigned a scale factor. The raw data were then processed (31) and 644 unique reflections were accepted as being statistically above background on the basis that $\sigma(I)/CI$ was less than 0.05 with P = 0.00. Lorentz-polarization corrections were made, but no corrections for absorption were made (μ = 23 cm^{-1}).

The coordinates of the copper and chlorine atoms were found from a three-dimensional Patterson synthesis (33). After three cycles of full-matrix least-squares (28) refinement, the conventional R value was 0.24. From an electron density map (26) phased on these atoms, the remaining non-hydrogen atoms were located. Four cycles of full-matrix least-squares refinement resulted in a conventional R value of 0.14. At this point the weighting scheme of Ibers (25), previously described, was introduced. Varying all atomic coordinates, individual isotropic temperature factors and two scale factors gave an R_1 of 0.13 and an R_2 of 0.12. Anisotropic temperature factors were then computed for the copper and chlorine atoms. The refinement was continued, varying all atomic coordinates, anisotropic temperature factors for the copper and chlorine atoms and the two scale factors, until no parameter showed any significant change. The final R values are R_1 = 0.089 and

R_2 = 0.081. The final structural parameters are listed in Table 11 and the final observed and calculated structure factors are listed in Table 12.

Table 11. Positional and Thermal Parameters for Cu(SALPA)Cℓ

Atom	x	y	z	B,A^2 or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	-0.0489(3)	0.0291(3)	0.1447(3)	38(4)	29(2)	31(3)	14(4)	-36(2)	-6(3)
Cℓ	0.1070(7)	0.1362(5)	0.2596(6)	107(12)	19(6)	67(8)	-13(6)	-49(7)	4(5)
O2	-0.1208(15)	0.0428(13)	-0.0250(12)	1.7(5)					
C3	-0.2653(26)	0.0872(19)	-0.0463(22)	2.1(8)					
C4	-0.2764(25)	0.1008(19)	-0.1813(21)	1.8(7)					
C5	-0.4255(27)	0.1448(20)	-0.2096(22)	2.2(8)					
C6	-0.5425(28)	0.1681(20)	-0.1137(25)	2.6(8)					
C7	-0.5271(24)	0.1531(19)	0.0165(22)	1.9(8)					
C8	-0.3738(22)	0.1101(17)	0.0501(19)	0.8(6)					
C9	-0.3750(24)	0.1036(18)	0.1868(20)	1.5(7)					
N10	-0.2478(19)	0.0778(14)	0.2414(16)	1.5(6)					
C11	-0.2684(25)	0.0743(18)	0.3876(21)	1.9(8)					
C12	-0.2822(26)	-0.0454(23)	0.4444(23)	3.0(9)					
C13	-0.1302(25)	-0.1104(19)	0.4050(21)	2.0(8)					
O14	-0.0955(17)	-0.1163(13)	0.2635(15)	2.7(6)					

Anisotropic temperature factors expressed as

$\exp[-(\beta_{11}h^2 = \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)] \times 10^4$.

Table 12. Observed and Calculated Structure Factors for Cu(SALPA)Cℓ

H	K	FO	FC
	L=-8		
1	0	46	47
2	0	27	22
3	0	37	48
4	0	32	21
5	0	44	40
6	0	44	46
7	0	33	24
1	2	25	24
4	2	28	20
5	2	30	24
6	2	31	30
7	2	29	26
2	3	26	30
5	3	28	30
7	4	30	21
1	5	53	59
2	5	40	31
3	5	48	52
4	5	38	31
5	5	29	26
7	5	28	6
1	7	52	52
2	7	38	32
3	7	36	32
4	7	41	42
1	9	30	21
4	9	29	21
	L=-7		
1	1	86	92
2	1	52	62
6	1	29	31
1	2	41	45
2	2	30	44
5	2	29	23
6	2	33	38
1	3	44	44
2	3	41	42
3	3	40	40
7	3	28	23
2	4	39	43
3	4	39	44
5	4	31	35
6	4	30	25
3	5	39	45
1	6	33	34
2	6	38	34
3	6	46	49
4	6	35	36
6	6	27	17
5	7	27	18
3	8	31	24
4	8	51	67
5	8	31	18
	L=-6		
1	0	30	31
2	0	70	74
3	0	64	71
4	0	51	52
5	0	59	73
6	0	30	13
2	1	29	30
3	1	33	32
4	1	25	20
1	2	62	67
2	2	76	82
3	2	47	47
4	2	34	38
5	2	30	23
3	3	42	47
4	3	27	21
1	4	82	88
2	4	53	53
3	4	30	27
1	5	41	38
2	5	39	41
6	5	27	14
7	5	36	40
1	6	28	24
1	7	34	36
2	7	25	23
4	7	27	31
6	7	30	26
7	7	33	37
1	8	28	24
4	8	29	27
4	9	32	32
	L=-5		
5	1	37	36
6	1	32	21
7	1	34	44
4	2	22	10
2	3	24	20
3	3	30	26
4	3	33	36
5	3	29	19
6	3	40	41
7	3	34	23
1	4	42	37
2	4	40	42
3	4	34	34
1	5	31	27
2	5	27	28
3	5	25	24
4	5	26	22
5	5	28	26
6	5	29	30
1	6	64	66
2	6	38	29
3	6	35	33
2	7	35	36
3	7	27	20
1	8	39	43
3	8	27	20
4	8	29	28
	L=-4		
H	K	FO	FC
7	0	27	17
4	1	40	38
5	2	29	23
6	2	26	18
7	2	31	27
3	3	49	49
4	3	48	47
5	3	31	30
4	4	29	25
5	4	42	41
6	4	38	40
7	4	33	34
4	5	25	17
5	5	39	38
6	5	35	32
7	5	33	35
1	6	24	21
1	7	36	37
2	7	33	30
3	7	28	20
4	7	33	28
5	7	34	33
6	7	36	39
7	7	29	22
2	8	27	22
1	9	52	55
2	9	56	61
3	9	48	50
4	9	37	40
5	9	34	33
6	9	28	21
	L=-3		
5	1	32	35
7	2	25	24
4	3	52	55
5	3	24	19
4	4	40	36
5	4	32	33
6	4	35	40
7	4	36	39
4	5	27	23
5	5	28	27
3	6	27	22
4	6	41	43
5	6	47	45
6	6	48	52
7	6	37	38
H	K	FO	FC
1	7	40	42
2	7	26	30
3	7	35	35
5	8	3_	27
6	8	34	33
7	8	33	31
	L=-2		
5	0	38	42
6	0	40	44
7	0	34	35
7	1	34	35
5	2	58	62
6	2	58	64
7	2	26	22
7	3	39	40
4	4	86	89
5	4	77	82
6	4	44	46
3	6	24	18
5	6	35	33
1	7	50	52
2	7	25	23
3	7	24	24
4	7	28	25
1	8	40	41
5	8	29	24
1	9	58	64
2	9	56	57
3	9	45	42
4	9	34	33
5	9	28	23
6	9	30	27
7	9	36	36
	L=-1		
5	1	55	57
6	1	66	70
7	1	51	52

Table 12. (Continued)

H	K	FO	FC
7	2	33	35
5	3	50	53
6	3	32	33
5	4	49	50
4	5	35	26
5	5	42	44
7	5	27	29
3	6	60	59
4	6	71	72
5	6	45	45
2	7	28	23
7	7	32	31
1	8	83	83
2	8	75	78
3	8	45	43
4	8	41	39
2	9	27	23
	L=	0	
6	0	62	68
6	1	40	41
6	2	31	28
5	3	52	53
6	3	45	46
5	4	29	28
4	5	64	62
5	5	52	52
2	7	107	105
3	7	76	80
4	7	54	55
5	7	31	28
6	7	29	26
7	7	29	25
0	8	41	36
1	8	31	27
2	8	29	27
4	8	48	47
1	9	27	23
3	9	42	43
5	9	30	29
6	9	46	52
7	9	45	49
	L=	1	
6	1	51	52
6	2	30	23
5	3	52	47
7	4	30	28
4	5	35	34
5	5	29	21
5	6	25	21
7	6	32	35
6	7	27	19
7	7	30	19
0	8	49	52
1	8	75	71
4	8	34	32
5	8	43	45
6	8	32	34
7	8	32	32
2	9	25	17
3	9	39	41
	L=	2	
6	0	116	123
7	0	64	67
5	2	43	42
6	2	67	69
7	2	56	59
5	3	46	40
6	3	30	24
5	4	25	22
7	4	42	40
4	5	70	63
7	5	32	29
4	6	50	50
5	6	42	43
2	7	46	42
3	7	71	64
4	7	60	59
0	8	43	43
1	8	27	19
4	8	40	40
5	8	35	32
6	8	31	23
0	9	50	55
1	9	29	27
3	9	26	22
4	9	33	25
	L=	3	
6	1	30	22
7	1	41	39
5	2	62	56
6	2	32	26
5	3	40	35
6	3	48	47
4	4	37	34
5	4	36	34
6	4	47	43
7	4	29	19
5	5	40	37
6	5	35	32
7	5	34	32
3	6	32	27
4	6	37	33
5	6	35	30
6	6	51	50
7	6	33	33
1	7	23	13
2	8	36	35
3	8	53	55
4	8	56	61
5	8	66	68
6	8	40	40
	L=	4	
5	0	68	64
6	0	33	25
5	2	38	34
2	3	30	20
3	3	41	35
4	3	45	37
5	3	30	26
6	3	28	21
7	3	36	28
0	4	94	98
1	4	81	82
2	4	65	57
3	4	41	37
0	5	52	52
1	5	42	40
2	5	55	48
4	5	31	29
5	5	51	49
6	5	64	65
7	5	52	56
2	6	30	27
3	6	36	33
4	6	39	35
0	7	33	33
1	7	29	26
4	7	40	40
5	7	45	46
6	7	50	52
7	7	37	40
0	8	29	21
3	8	26	18
2	9	29	26
3	9	37	35
4	9	42	40
5	9	37	34
	L=	5	
0	1	36	31
1	1	48	46
2	1	106	96
3	1	92	90
4	1	69	65
5	1	58	58
6	1	38	38
1	2	69	58
3	2	42	34
4	2	31	25
5	2	27	19
2	3	41	36
3	3	55	46
4	3	63	60
5	3	55	57
6	3	59	63
7	3	37	41
0	4	73	73
1	4	67	68
2	4	42	39
5	4	31	22
6	4	29	19
0	5	30	28
3	5	49	40
4	5	40	39
5	5	38	37
6	5	33	32
7	5	31	28
0	6	78	87
1	6	51	57
2	6	47	46
5	6	35	29
6	6	32	28
1	7	34	36
3	7	37	33
0	8	39	43
1	8	37	34
2	8	39	39
3	8	46	48
	L=	6	
5	0	41	36
7	0	57	67
2	1	42	39
3	1	47	36
4	1	26	17
1	2	32	27
4	2	55	49
5	2	39	38
6	2	36	38
7	2	38	43
0	3	29	23
1	3	63	64
2	3	65	65
3	3	54	49

Table 12. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
2	5	35	34	1	1	58	61	5	6	41	49	2	2	42	41
3	5	28	25	2	1	55	54	6	6	36	40	3	2	48	50
4	5	32	27	3	1	48	48	0	7	29	24	4	2	47	48
5	5	30	31	5	1	35	29	1	7	42	44	5	2	48	44
6	5	41	39	0	2	26	18	2	7	30	30	6	2	35	30
0	7	34	39	4	2	31	23	7	7	36	33	1	3	26	16
1	7	40	39	7	2	43	40	1	8	34	28	2	3	27	17
2	7	42	44	0	3	46	45	2	8	34	32	3	3	37	31
3	7	41	41	1	3	31	31	5	8	31	30	7	3	37	35
5	7	46	46	2	3	25	17	6	8	37	41	2	4	32	28
6	7	31	27	3	3	34	28					3	4	47	50
3	8	28	23	5	3	41	31		L=	8		4	4	48	47
4	8	33	27	3	4	41	39					5	4	58	59
0	9	39	42	4	4	51	51	0	0	47	49	6	4	31	25
1	9	55	62	7	4	40	40	1	0	63	61	0	7	38	36
2	9	63	70	0	5	36	37	2	0	51	53	1	8	29	23
3	9	40	48	1	5	32	29	3	0	31	28	0	9	38	41
4	9	32	33	2	5	29	29	4	0	37	39	1	9	32	31
5	9	30	24	4	5	35	24	6	0	42	34	2	9	31	30
				5	5	30	25	2	1	27	20	6	9	38	41
	L=	7		2	6	33	30	3	1	31	25	7	9	38	40
				3	6	58	61	0	2	31	21				
0	1	71	71	4	6	36	40	1	2	41	39				

Solution of the Structure of the Cobalt Trimer (35)

Crystals suitable for single-crystal X-ray work were obtained directly from the preparation of the compound. An octahedral-shaped crystal with an average trigonal-face to trigonal-face distance of approximately 0.3 mm was mounted and precession photographs were taken. Precession camera photographs indicated that the crystal was monoclinic with the systematic absence of all reflections with $h + k = 2n+1$. These absences were consistent with space groups C2 or C2/m. After these data had been collected, the crystal and goniometer head were transferred to the diffractometer where final adjustments were made (23). Fourteen reflections were scanned and used as input data for the least-squares program (24). The refined unit cell constants obtained by this least-squares method are a = 14.984(6)Å, b = 8.617(4)Å, c = 11.285(6)Å and β = 116.68(3)°. The density calculated for two trimeric units per unit cell, 1.68 g/cm^3, agreed well with the experimental value, 1.66 g/cm^3, obtained by the flotation method in a mixture of carbon tetrachloride and methylene iodide. The data were collected as described earlier. A total of 1262 reflections were collected using a 60-second background count and a 2° scan. The reflections with $h + k = 2n+1$ were not collected since symmetry requirements forced them to be absent. The reflections collected were in the region between 0-10 in h, 0-10 in k and -10 to +10 in l. A standard reflection was measured about every four hours to check for electronic changes and crystal decomposition. No significant changes were noticed in the intensity of the standard reflection during the collection of the data.

After processing the data, 830 reflections were accepted (31) as being statistically above background on the basis that $\sigma(I)/CI$ was less than 0.09 with P = 0.01. Lorentz-polarization corrections were then calculated but no corrections were made for absorption (μ = 20 cm^{-1}).

Although both space groups C2 and C2/m have two-fold positions, the 2/m symmetry of the two-fold positions in C2/m was not consistent with any reasonable structure for the trimer. Thus, C2 was chosen as the correct space group and was confirmed as being correct by the successful refinement of the structure.

Since the origin in the y direction of space group C2 is not fixed by symmetry, the cobalt atom of the two-fold set (2a) was placed at the origin of the unit cell. From a three-dimensional Patterson synthesis (33), coordinates for the cobalt atom of the fourfold general set (4c) were obtained. Successive structure factor (28) and Fourier calculations (26) were used to locate the remaining non-hydrogen atoms of the structure. Since the three cobalt atoms are essentially in the xz plane, a false mirror plane was created. The effect of this mirror plane was noticed since the oxygen atoms of the acetates were disordered and the disordered oxygen atoms were almost related by the false mirror plane. With all reflections weighted at unity, individual isotropic temperature factors and no corrections for anomalous dispersion (32), the conventional R value, R, was 0.11. When corrections for anomalous dispersions ($\Delta f'$ and $\Delta f''$) were made and anisotropic temperature factors calculated for the cobalt atoms, the conventional R value was 0.088. On the final cycles of refinement all atomic

coordinates, anisotropic temperature factors for the cobalt atoms and the scale factor were varied until no parameter showed any significant change. The final structural parameters are given in Table 13 and the final observed and calculated structure factors are given in Table 14.

Table 13. Final Positional and Thermal Parameters for the Cobalt Trimer

Atom	x	y	z	B,A^2 or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co1	0	0	0	48(3)	120(5)	68(4)	0	24(3)	0
Co2	0.0860(2)	-0.0010(12)	0.2577(2)	28(2)	58(3)	29(2)	-33(3)	7(1)	-28(3)
O1	0.1289(13)	0.0867(20)	0.1390(16)	3.0(4)					
O2	0.0477(14)	-0.1829(19)	0.1385(16)	2.7(4)					
O3	-0.0434(14)	0.0804(23)	0.1389(18)	3.8(5)					
N1	0.1037(21)	0.1791(35)	0.3604(25)	5.3(8)					
N2	0.2255(19)	-0.0778(30)	0.3628(23)	4.5(7)					
N3	0.0294(21)	-0.1216(32)	0.3615(26)	5.0(7)					
C11	0.2888(18)	-0.0287(30)	0.3143(21)	3.5(7)					
C12	0.2231(22)	-0.0292(39)	0.1633(25)	5.1(9)					
C21	0.0062(24)	0.2560(34)	0.3231(29)	3.5(8)					
C22	-0.0397(28)	0.2369(37)	0.1721(35)	4.6(1.0)					
C31	0.0214(24)	-0.2898(36)	0.3084(30)	3.7(8)					
C32	-0.0212(25)	-0.2707(33)	0.1593(31)	3.7(9)					
CA1	0.7213(13)	-0.0299(18)	0.1634(13)	0.8(7)					
CA2	0.7689(15)	0.0122(30)	0.3055(17)	2.0(5)					
O1A	0.7134(38)	0.0263(72)	0.3607(47)	7.5(1.9)					
C1AB	0.7561(35)	-0.1057(50)	0.3797(39)	4.3(1.1)					
O2A	0.8145(29)	-0.1276(39)	0.3600(31)	2.8(8)					
O2AB	0.8513(33)	0.0513(47)	0.3729(41)	4.9(1.2)					

Table 14. Observed and Calculated Structure Factors for the Cobalt Trimer

H	K	FO	FC
	L=-10		
2	0	21	22
4	0	30	30
6	0	44	44
8	0	69	71
1	1	30	27
5	1	32	36
7	1	49	49
9	1	31	30
2	2	17	21
4	2	19	19
6	2	24	25
8	2	44	44
5	3	34	37
7	3	44	43
9	3	25	24
4	4	29	26
6	4	44	44
8	4	50	49
5	5	35	38
7	5	45	42
9	5	23	21
0	6	18	13
2	6	19	19
4	6	21	16
6	6	34	33
8	6	31	33
1	7	18	15
5	7	23	25
7	7	32	30
9	7	20	15
2	8	17	14
6	8	22	20
8	8	24	21
1	9	22	15
5	9	22	14
2	10	18	12
4	10	18	9
6	10	21	16
10	10	21	5
	L=-9		
2	0	63	67
4	0	55	54
6	0	45	46
8	0	31	34
1	1	23	25
3	1	65	66
5	1	57	59
2	2	49	54
4	2	46	45
6	2	46	53
8	2	26	31
1	3	19	17
3	3	38	43
5	3	41	48
9	3	24	25
2	4	35	38
4	4	37	41
6	4	33	38
8	4	21	22
10	4	23	20
1	5	24	19
3	5	44	47
5	5	47	51
0	6	17	12
2	6	34	33
4	6	45	42
6	6	30	30
10	6	22	17
1	7	20	12
3	7	29	32
5	7	33	31
0	8	17	15
2	8	20	19
4	8	28	28
6	8	20	15
1	9	17	14
3	9	23	22
5	9	21	20
7	9	19	6
2	10	23	15
4	10	24	19
	L=-8		
2	0	68	71
4	0	25	23
6	0	42	40
8	0	28	29
1	1	85	88
3	1	43	45
5	1	26	31
7	1	27	26
2	2	80	82
4	2	18	26
6	2	21	14
10	2	36	37
1	3	44	48
3	3	32	31
5	3	24	24
7	3	25	29
2	4	42	48
6	4	21	20
8	4	26	27
10	4	31	29
1	5	47	47
3	5	36	37
2	6	53	54
4	6	18	8
10	6	29	27
1	7	31	33
3	7	22	19
2	8	26	28
6	8	19	16
1	9	28	28
3	9	22	14
2	10	22	22
4	10	19	3
	L=-7		
4	0	25	27
8	0	64	62
10	0	42	42
1	1	29	23
3	1	27	28
5	1	32	31
7	1	40	46
9	1	57	58
2	2	24	25
4	2	38	37
8	2	67	71
10	2	57	65
1	3	21	21
3	3	26	26
7	3	43	46
9	3	71	71
2	4	20	23
8	4	49	48
10	4	52	56
3	5	20	22
7	5	20	22
9	5	36	37
2	6	20	23
8	6	34	34
10	6	36	36
3	7	19	17
7	7	26	20
9	7	42	39
2	8	19	18
4	8	19	19
8	8	30	28
10	8	30	28
3	9	22	20
9	9	24	26
8	10	23	19
10	10	22	16
	L=-6		
4	0	108	100
6	0	123	121
8	0	42	43
1	1	22	31
3	1	22	18
5	1	101	101
7	1	90	91
9	1	30	28
2	2	71	68
4	2	54	53
6	2	108	105
8	2	53	54
1	3	37	37
3	3	20	14
5	3	81	79
7	3	84	87
9	3	33	31
4	4	47	47
6	4	64	67
8	4	41	42
1	5	27	29
5	5	27	29
7	5	31	35
9	5	22	16
2	6	25	30
4	6	18	18
6	6	25	28
1	7	22	21
5	7	35	37
7	7	38	38
9	7	21	23
4	8	27	26
6	8	42	41
8	8	32	28
1	9	21	21
5	9	26	26
7	9	33	30
6	10	25	24
	L=-5		
2	0	44	45
4	0	99	99
6	0	36	32
10	0	52	56
1	1	61	54
3	1	92	90
5	1	93	94
7	1	24	36
9	1	36	37
2	2	104	97
4	2	133	129

Table 14. (Continued)

H	K	FO	FC
10	2	34	40
1	3	56	53
3	3	113	112
5	3	8	78
9	3	29	29
2	4	82	82
4	4	85	81
6	4	28	30
10	4	24	20
1	5	44	44
3	5	66	67
5	5	40	37
9	5	25	24
2	6	52	54
4	6	33	37
6	6	19	17
8	6	23	21
1	7	31	33
3	7	39	43
5	7	26	26
9	7	27	26
2	8	44	44
4	8	36	40
6	8	21	17
8	8	22	19
10	8	23	17
1	9	27	19
3	9	34	36
5	9	29	28
9	9	22	19
2	10	20	20
4	10	25	23
6	10	21	10
8	10	21	13
10	10	22	12
L=-4			
2	0	80	79
4	0	28	32
6	0	34	29
8	0	31	32
10	0	63	64
1	1	57	57
3	1	57	64
5	1	36	44
7	1	29	32
9	1	23	30
2	2	117	107
6	2	81	70
10	2	26	18
1	3	137	134
3	3	52	49
5	3	31	27
7	3	31	28
9	3	20	17
2	4	82	80
4	4	27	18
6	4	39	43
8	4	2	19
10	4	25	23
1	5	87	91
3	5	29	23
5	5	24	24
7	5	30	28
2	6	42	42
6	6	43	46
1	7	55	56
3	7	24	24
5	7	19	22
9	7	21	17
2	8	32	33
6	8	30	27
1	9	33	33
3	9	19	15
7	9	19	16
2	10	24	18
6	10	20	15
L=-3			
4	0	23	15
6	0	56	48
8	0	79	84
10	0	112	114
3	1	55	48
5	1	22	30
7	1	60	54
9	1	99	102
2	2	46	46
4	2	54	50
6	2	40	56
8	2	54	56
10	2	66	59
3	3	46	48
5	3	27	33
7	3	54	53
9	3	57	64
2	4	34	34
2	4	34	34
2	4	34	34
4	4	60	54
6	4	35	34
8	4	68	64
10	4	53	53
3	5	40	41
5	5	20	21
7	5	59	54
9	5	67	67
2	6	17	16
4	6	30	32
6	6	25	26
8	6	49	51
10	6	36	39
3	7	21	22
7	7	32	34
9	7	36	43
2	8	18	16
6	8	21	12
8	8	32	33
10	8	24	29
3	9	18	19
7	9	21	16
9	9	29	29
8	10	21	22
10	10	21	21
L=-2			
6	0	80	81
8	0	31	22
10	0	20	15
1	1	28	23
3	1	32	39
5	1	83	82
7	1	78	77
9	1	34	34
0	2	60	50
2	2	123	108
4	2	65	64
6	2	129	140
8	2	53	49
10	2	21	24
1	3	57	48
3	3	20	27
5	3	80	79
7	3	55	53
9	3	21	19
2	4	28	29
4	4	33	34
6	4	103	101
8	4	25	28
1	5	33	37
3	5	36	34
5	5	118	114
7	5	95	90
9	5	27	27
2	6	20	21
4	6	59	55
6	6	113	112
8	6	40	39
1	7	24	26
5	7	49	52
7	7	39	42
6	8	36	41
5	9	31	33
7	9	27	29
0	10	18	18
4	10	23	18
6	10	28	28
8	10	21	19
L=-1			
8	0	57	56
5	1	66	69
7	1	28	37
9	1	40	42
0	2	32	47
4	2	86	78
6	2	42	47
8	2	33	29
1	3	67	68
3	3	86	85
5	3	63	51
9	3	29	32
2	4	81	79
4	4	85	88
6	4	24	23
8	4	36	37
10	4	29	31
1	5	55	55
3	5	105	103
5	5	67	69
9	5	38	39
2	6	70	64
4	6	96	91
6	6	24	26
10	6	24	21
1	7	26	30
3	7	68	65
5	7	42	37
0	8	18	15
2	8	32	33
4	8	37	37
1	9	18	18
3	9	37	38
5	9	19	17
2	10	32	31
4	10	30	26
L= 0			
4	0	122	112
6	0	46	45
8	0	26	23

Table 14. (Continued)

H	K	FO	FC
10	0	39	40
5	1	58	56
7	1	34	20
9	1	28	25
6	2	88	73
10	2	42	43
1	3	86	80
5	3	33	34
9	3	36	33
0	4	130	130
2	4	63	67
4	4	31	33
6	4	39	35
8	4	20	20
10	4	51	56
1	5	55	63
3	5	25	26
5	5	56	52
7	5	28	28
0	6	58	61
2	6	25	31
4	6	20	13
6	6	42	43
10	6	34	35
1	7	55	53
3	7	28	24
9	7	21	15
0	8	53	55
2	8	29	25
10	8	29	28
1	9	29	30
5	9	22	23
9	9	20	10
0	10	36	35
2	10	21	18
6	10	20	20
L= 1			
4	0	44	48
8	0	82	80
10	0	27	22
3	1	60	55
7	1	83	77
9	1	65	64
2	2	25	21
4	2	40	44
6	2	39	52
8	2	87	88
10	2	51	51
3	3	35	32
5	3	22	27
7	3	57	54
9	3	76	74
0	4	42	51
2	4	31	37
6	4	32	28
8	4	61	65
10	4	48	49
1	5	17	28
3	5	38	39
7	5	36	37
9	5	49	54
0	6	21	24
2	6	36	40
4	6	27	31
8	6	36	39
10	6	34	37
3	7	37	39
7	7	24	24
9	7	36	39
4	8	22	24
6	8	20	18
8	8	31	36
10	8	28	33
3	9	24	24
7	9	26	30
9	9	27	30
8	10	21	23
10	10	22	22
L= 2			
4	0	112	103
6	0	109	110
8	0	46	49
3	1	59	62
5	1	137	131
7	1	82	77
2	2	30	35
4	2	100	93
6	2	114	107
8	2	44	43
10	2	27	31
1	3	40	43
3	3	37	34
5	3	96	95
7	3	72	72
0	4	85	71
2	4	26	37
4	4	45	49
6	4	62	63
8	4	38	37
10	4	25	22
3	5	32	28
5	5	46	46
7	5	34	36
0	6	30	31
2	6	19	13
4	6	34	36
6	6	29	32
8	6	22	22
10	6	22	30
1	7	28	26
3	7	20	27
5	7	36	39
7	7	31	37
0	8	30	30
4	8	37	37
6	8	36	39
8	8	26	22
1	9	20	19
3	9	23	18
5	9	36	37
7	9	28	31
4	10	25	25
6	10	26	28
L= 3			
2	0	55	56
4	0	101	100
1	1	82	80
3	1	96	94
5	1	55	53
0	2	59	71
2	2	104	98
4	2	106	104
8	2	29	30
1	3	100	101
3	3	130	125
5	3	41	46
9	3	26	24
0	4	41	51
2	4	94	94
4	4	67	65
1	5	55	53
3	5	61	61
0	6	35	39
2	6	62	64
4	6	33	35
1	7	51	54
3	7	52	55
5	7	22	23
9	7	21	21
0	8	26	29
2	8	46	46
4	8	37	39
8	8	23	23
10	8	21	19
1	9	28	26
3	9	33	36
5	9	25	19
7	9	22	19
0	10	20	10
2	10	27	26
4	10	24	28
8	10	22	18
L= 4			
2	0	60	52
4	0	70	72
6	0	26	25
10	0	47	48
1	1	46	45
3	1	22	17
5	1	38	40
7	1	22	24
9	1	34	36
0	2	96	93
2	2	114	105
4	2	34	42
6	2	20	15
10	2	53	54
1	3	107	105
5	3	30	34
7	3	26	36
0	4	113	107
2	4	41	44
4	4	30	43
10	4	32	34
1	5	71	72
5	5	20	9
9	5	33	31
0	6	76	77
2	6	37	34
6	6	21	18
8	6	20	12
10	6	29	36
1	7	50	52
5	7	23	24
7	7	21	20
0	8	45	48
2	8	28	21
4	8	22	27
6	8	23	24
8	8	21	9
10	8	24	24
1	9	31	35
5	9	22	19
0	10	22	26
2	10	20	12
4	10	21	15
6	10	22	17
10	10	23	22

Table 14. (Continued)

H	K	FO	FC
	L= 5		
2	0	24	30
4	0	24	22
6	0	35	31
8	0	38	38
10	0	37	37
3	1	29	27
5	1	21	29
7	1	41	49
9	1	45	46
0	2	22	20
2	2	27	28
4	2	28	36
6	2	47	52
8	2	45	47
10	2	33	37
1	3	35	30
3	3	44	47
7	3	45	45
9	3	35	32
2	4	30	29
4	4	34	36
6	4	31	33
8	4	34	33
10	4	24	22
7	5	39	47
9	5	31	32
6	6	36	37
8	6	38	40
10	6	22	25
1	7	24	24
3	7	19	20
7	7	36	34
9	7	28	26
8	8	27	26
7	9	24	23
2	10	19	14
6	10	22	14
8	10	25	24
10	10	24	17
	L= 6		
2	0	35	24
4	0	79	86
6	0	40	46
8	0	29	28
10	0	24	16
3	1	43	45
5	1	46	48
7	1	33	40
9	1	20	11
0	2	28	29
2	2	26	27
4	2	58	58
6	2	27	25
8	2	22	16
1	3	27	26
3	3	47	44
5	3	52	50
7	3	36	39
0	4	20	12
4	4	74	76
6	4	43	46
1	5	29	29
3	5	34	33
5	5	45	47
7	5	33	34
9	5	22	17
0	6	22	28
4	6	43	45
6	6	36	36
3	7	30	31
5	7	38	40
7	7	27	29
0	8	18	19
4	8	29	32
6	8	26	30
1	9	20	16
5	9	23	25
0	10	19	17
8	10	22	17
10	10	22	15
	L= 7		
0	0	66	62
2	0	85	88
4	0	50	54
1	1	62	70
3	1	65	67
9	1	23	17
0	2	44	44
2	2	54	53
4	2	33	36
1	3	58	61
3	3	44	48
5	3	25	24
0	4	48	47
2	4	52	51
4	4	45	48
1	5	46	46
3	5	44	45
5	5	26	24
0	6	28	32
2	6	33	36
4	6	32	35
8	6	21	21
1	7	33	36
3	7	28	34
7	7	21	19
9	7	22	14
0	8	24	26
2	8	28	29
4	8	22	22
6	8	21	17
8	8	23	16
1	9	24	22
3	9	28	23
5	9	22	17
7	9	23	15
0	10	21	15
2	10	24	25
4	10	23	16
6	10	24	18
8	10	22	17
	L= 8		
0	0	84	79
2	0	26	22
4	0	21	22
6	0	20	20
8	0	22	9
10	0	30	19
1	1	65	66
9	1	24	19
0	2	68	66
2	2	34	30
8	2	22	12
10	2	23	20
1	3	35	37
5	3	20	20
9	3	23	22
0	4	27	29
2	4	22	23
4	4	23	26
10	4	24	21
1	5	36	38
5	5	29	25
9	5	24	20
0	6	35	36
2	6	24	23
4	6	23	21
6	6	23	22
10	6	23	19
1	7	21	23
3	7	20	19
5	7	25	21
9	7	23	17
0	8	25	23
10	8	22	20
1	9	23	18
3	9	22	14
0	10	23	23
4	10	21	15
6	10	22	14
8	10	22	18
	L= 9		
2	0	29	28
6	0	26	24
8	0	36	36
1	1	24	23
3	1	21	22
7	1	33	31
9	1	23	22
6	2	26	20
8	2	32	32
5	3	21	13
7	3	33	30
9	3	26	26
2	4	20	21
6	4	24	19
8	4	29	32
10	4	23	14
1	5	20	19
7	5	27	21
9	5	23	21
2	6	21	21
8	6	25	24
3	7	21	17
7	7	23	22
9	7	24	20
6	8	23	20
8	8	24	23
10	8	26	15
1	9	24	14
5	9	23	18
7	9	22	20
9	9	25	16
0	10	23	11
2	10	21	17
4	10	24	11
6	10	23	19
10	10	26	15
	L=10		
0	0	38	37
4	0	30	29
6	0	31	32
1	1	21	19
3	1	31	26

Table 14. (Continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
5	1	40	38	5	3	34	36	4	6	25	23	6	8	21	18
7	1	25	13	2	4	21	21	6	6	25	22	3	9	21	19
0	2	19	20	4	4	24	24	8	6	21	15	5	9	27	22
2	2	26	16	6	4	27	26	3	7	22	19	0	10	21	12
4	2	32	33	10	4	22	12	5	7	25	24	2	10	22	15
6	2	36	36	3	5	22	21	0	8	20	13	4	10	23	19
3	3	23	27	5	5	30	28	4	8	25	22	10	10	24	14

Crystallographic Data for $Cu_4OCl_6(TPPO)_4 \cdot 2CH_3NO_2$

Well-shaped orange needle-like crystals were obtained from the preparation of the compound. A crystal was mounted along its long dimension and precession camera photographs were taken. These photographs indicated that the crystal was monoclinic with a = 13.79(2)Å, b = 26.67(3)Å, c = 22.50(3)Å and β = 113(1)°. The density calculated on the basis of four formula units per unit cell, 1.50 g/cm^3, was the same as the measured value obtained by the flotation method in a mixture of carbon tetrachloride and benzene. Systematic absence of the reflections with l = 2n+1 on the $h0l$ zone indicated that the space group was Pc or P2/c.

No intensity data were collected on this crystal and no attempt was made to solve the structure.

Crystallographic Data for $Cu_4OBr_6(TPPO)_4 \cdot 2CH_3NO_2$

Well-shaped octahedral crystals were obtained from the preparation of the compound. A crystal was mounted on one of the apices of the octahedron and precession camera photographs were taken. These photographs indicated that the crystal was cubic, space group P23, with a = 12.47(2)Å. The calculated density based on one formula unit per unit cell, 1.67 g/cm^3, agreed well with the experimental value, 1.69(2) g/cm^3, obtained by the flotation method in a mixture of carbon tetrachloride and methylene iodide.

A limited amount of intensity data, 127 reflections, were collected on a Buerger precession camera. The central oxygen, copper and bromine atoms were located from a three-dimensional Patterson synthesis

(33), but the structure never refined properly. The atomic positions, Table 15, are essentially the same as those found for the Cu_4OCl_6 unit in $Cu_4OCl_6(TPPO)_4$ by Bertrand (10). These structural parameters are reasonable but the R value of 0.42 with these atoms in the calculations discouraged any further attempts toward the solution of the structure.

Table 15. Approximate Structural Parameters for $Cu_4OBr_6(TPPO)_4 \cdot 2CH_3NO_2$

Atom	x	y	z
Ocnt	0	0	0
Cu	0.0899	0.0899	0.0899
Br	0.2421	0	0

Magnetic Studies

All of the magnetic susceptibilities were determined at room temperature by the Gouy method as previously described (36). The gram susceptibilities, χ_g, have been corrected for the susceptibilities of the glass tube and for the displaced air. Molar susceptibilities, χ_m, were obtained by correcting for the diamagnetism of the ligands and ions. The diamagnetic corrections of Lewis and Wilkins (37) were used. The magnetic moments, μ, were calculated using the equation

$$\mu = 2.84(\chi_m T)^{1/2}$$

where T is the absolute temperature. The results of the calculations are given in Table 16.

Table 16. Magnetic Moment Data

Compound	$\chi_g \times 10^6$	$\chi_m \times 10^6$	μ(Bohr Magnetons)
$[(CH_3)_4N]_4Cu_4OCl_{10}$	3.60	2162	2.20
$Cu_4OCl_6(TPPO)_4 \cdot 2CH_3NO_2$	3.75	1835	2.10
$Cu_4OBr_6(TPPO)_4 \cdot 2CH_3NO_2$	2.86	1675	2.00
$Cu_4OCl_6(PyO)_4$	7.76	1773	2.06
Cobalt Trimer	10.00	2317	2.36
Cu(PIA)	-0.15	69	0.41
Cu(mSALPA)	0.04	135	0.57
Cu(EIA)	6.59	1440	1.87
Cu(SALPA)Cl	1.20	332	1.06

Spectral Studies

The visible and near infrared spectra were recorded using a Cary model 14 spectrophotometer. One-centimeter matched quartz cells were used in all cases. The results of these determinations are given in Figures 2 through 7.

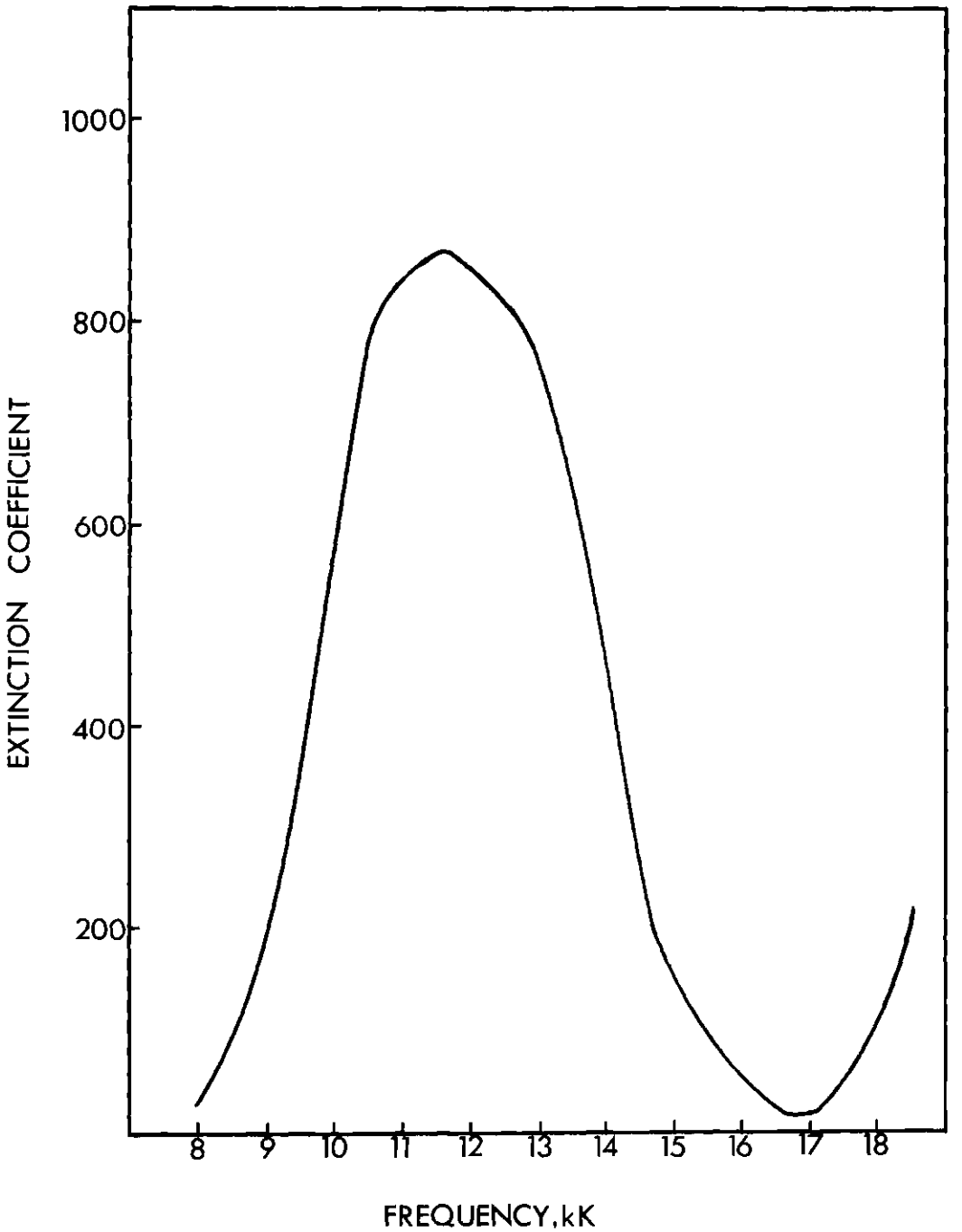


Figure 2. Solution Spectrum of $Cu_4OCl_6(PyO)_4$ in CH_3CN

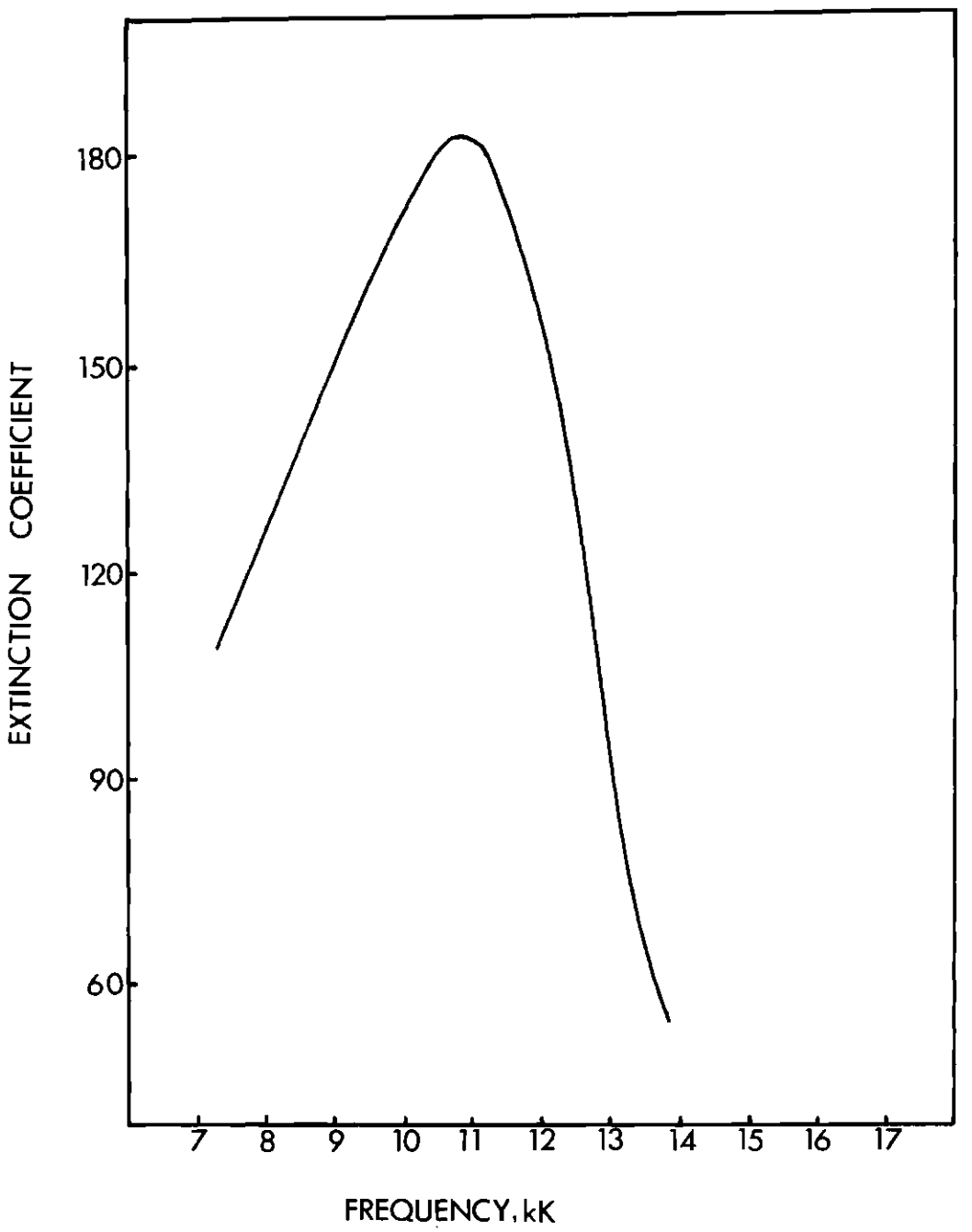


Figure 3. Solution Spectrum of $[(CH_3)_4]_4Cu_4OCl_{10}$ in CH_3NO_2

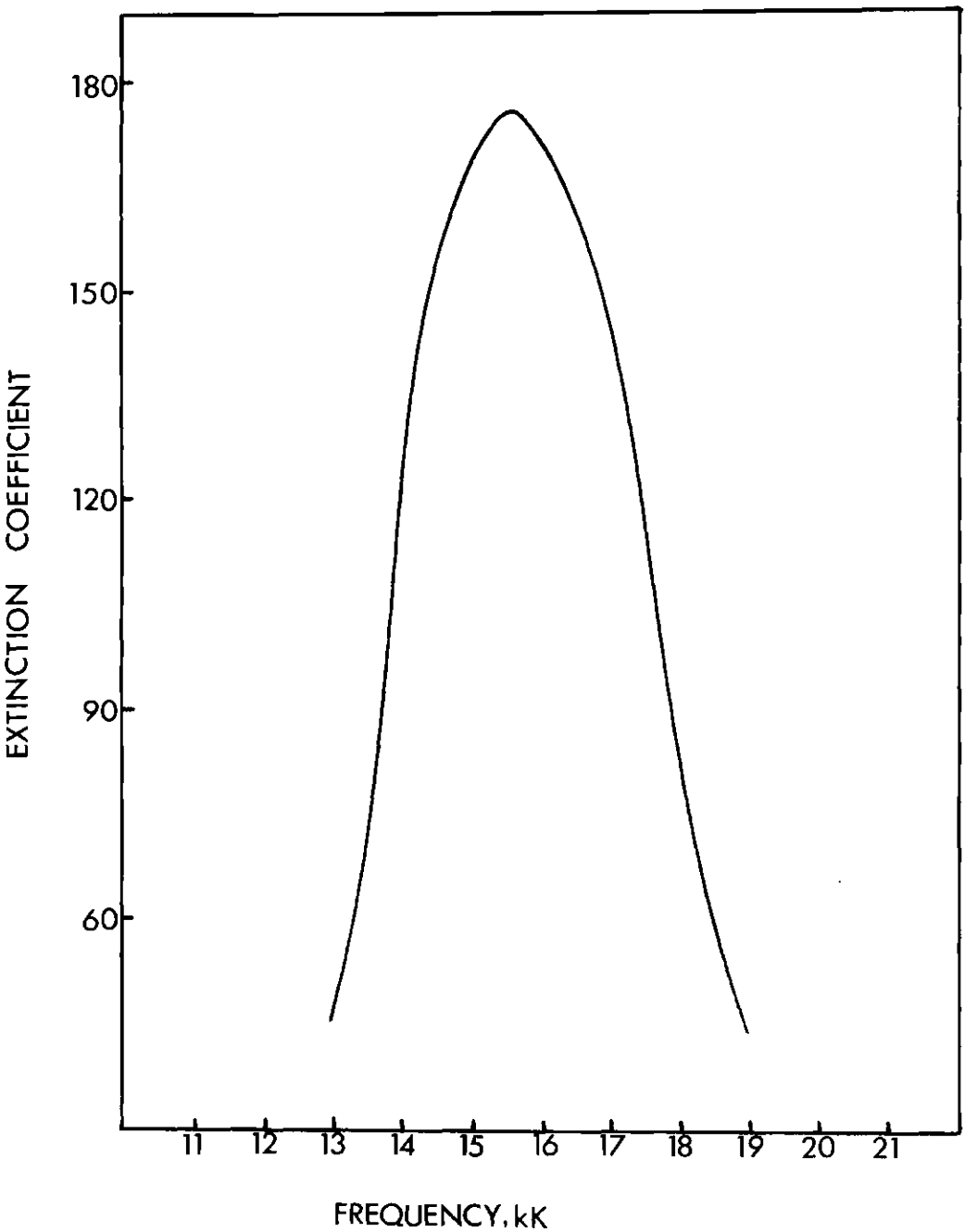


Figure 4. Solution Spectrum of Cu(EIA) in $CHCl_3$

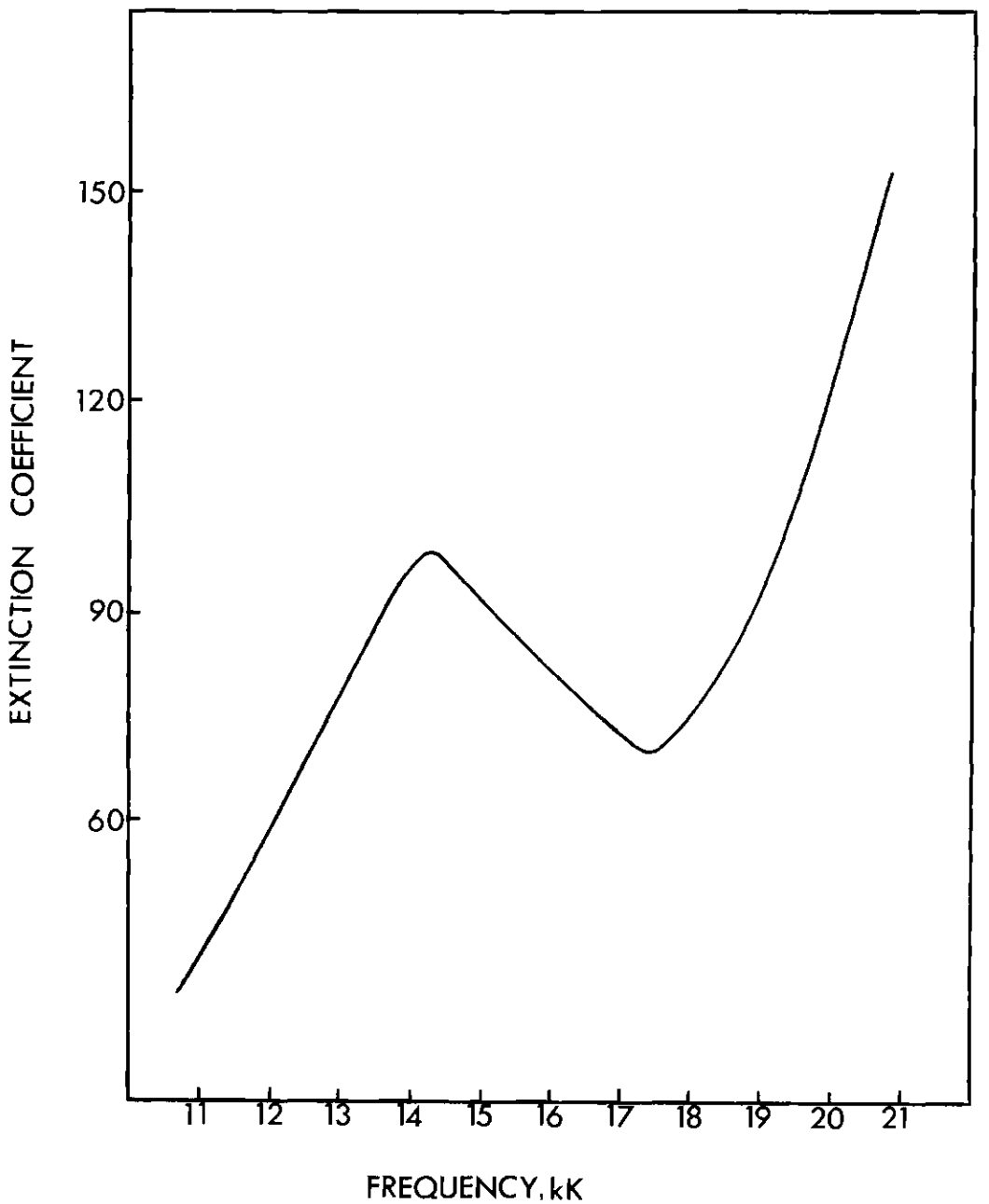


Figure 5. Solution Spectrum of Cu(SALPA)Cℓ in CH_3NO_2

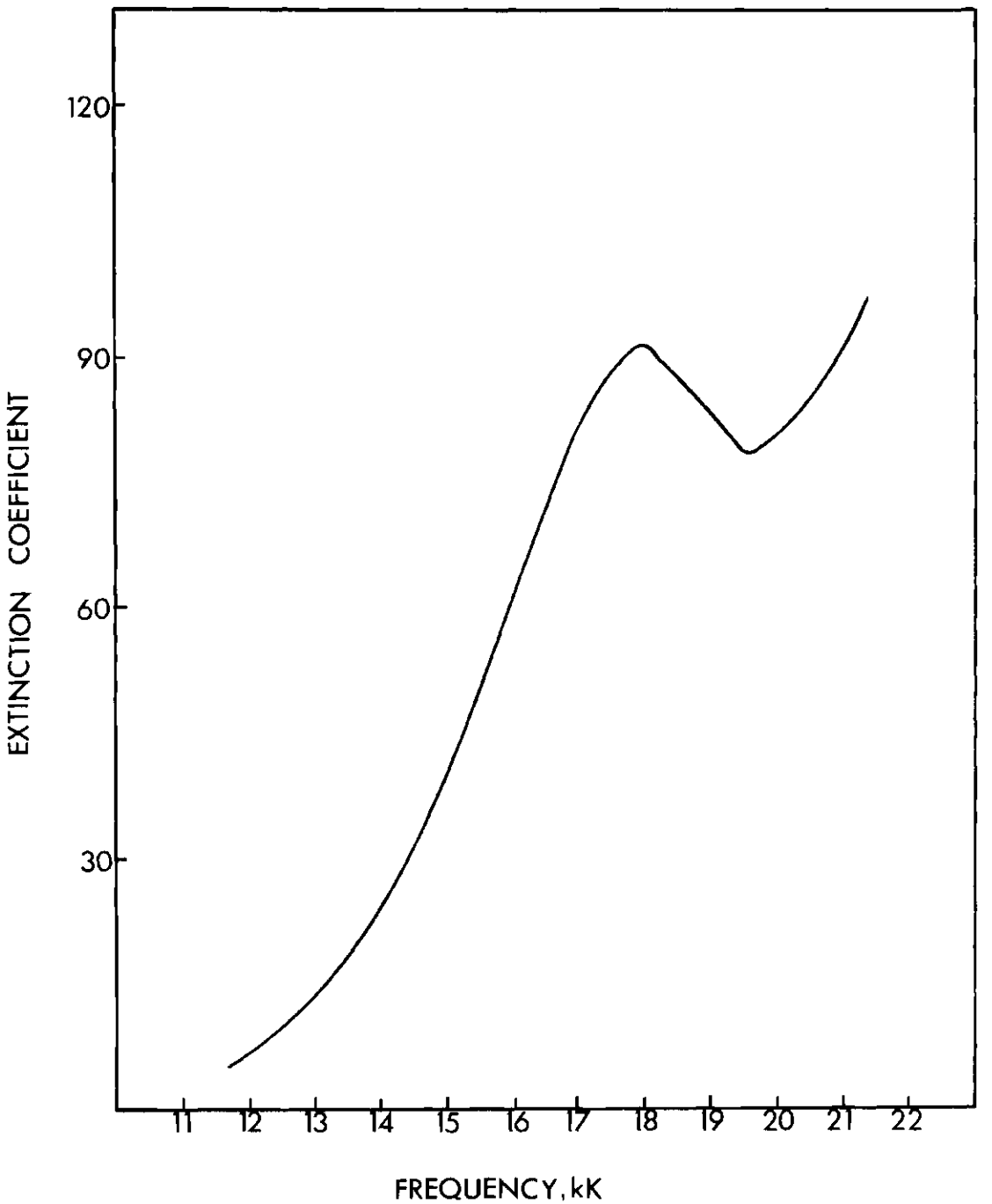


Figure 6. Solution Spectrum of Cu(PIA) in CH_3NO_2

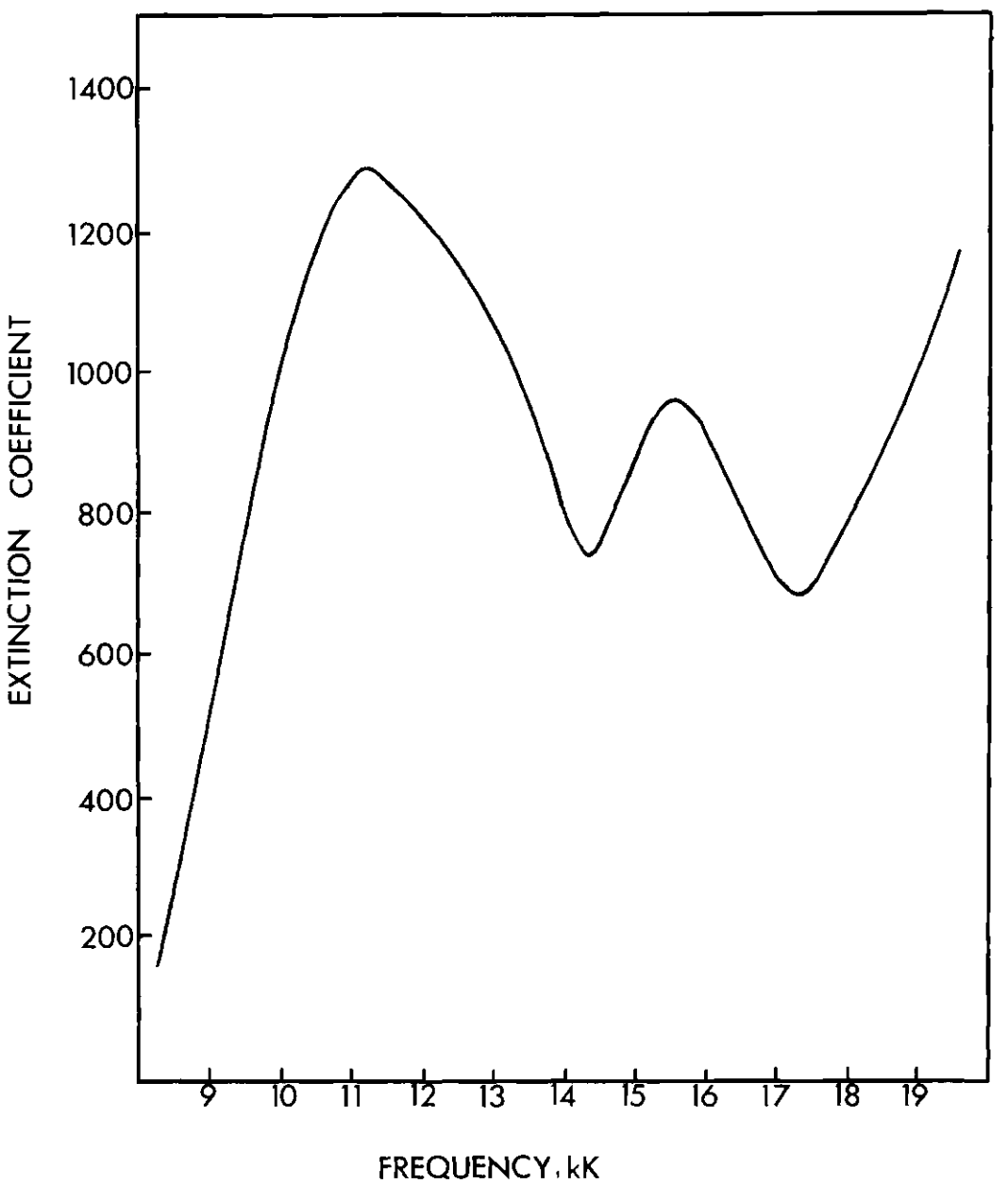


Figure 7. Solution Spectrum at $Cu_4OCl_6(TPPO)_4 \cdot 2CH_3NO_2$ in CH_3NO_2

CHAPTER III

RESULTS AND DISCUSSION

Structures

μ_4-oxo-hexa-μ-chlorotetra(chlorocuprate(II))anion

A perspective drawing of the structure is shown in Figure 8. The structure consists of a regular tetrahedron of Copper(II) atoms surrounding a central oxygen atom at the center of the tetrahedron. Chloride atoms bridge adjacent copper atoms along the six edges of the tetrahedron and form a regular octahedron around the central oxygen. The coordination of the copper is essentially trigonal bipyramidal with the equatorial positions being occupied by three of the bridging chlorides and the axial positions being occupied by the central oxygen and a chloride atom.

There are two independent polynuclear units of this type in the unit cell. The structure is analogous to that found for $Cu_4OCl_6(TPPO)_4$ (10), $Cu_4OCl_6(pyridine)_4$ (17) and $Mg_4OBr_6(C_4H_{10}O)_4$ (15). Interatomic distances and angles for the $Cu_4OCl_{10}^{-4}$ units are given in Table 17 and the bond distances and bond angles for the tetramethylammonium groups are given in Table 18. Although crystallographically independent, the only significant difference in the two anions is in the Cu-Cl_{ax} distances. This distance is 2.17Å for the origin ion and 2.25Å for the non-origin ion. The Cu-O distances, 1.95Å and 1.92Å, agree well with the values from previous structures of this type, 1.88Å to 1.92Å (10,15,17), and

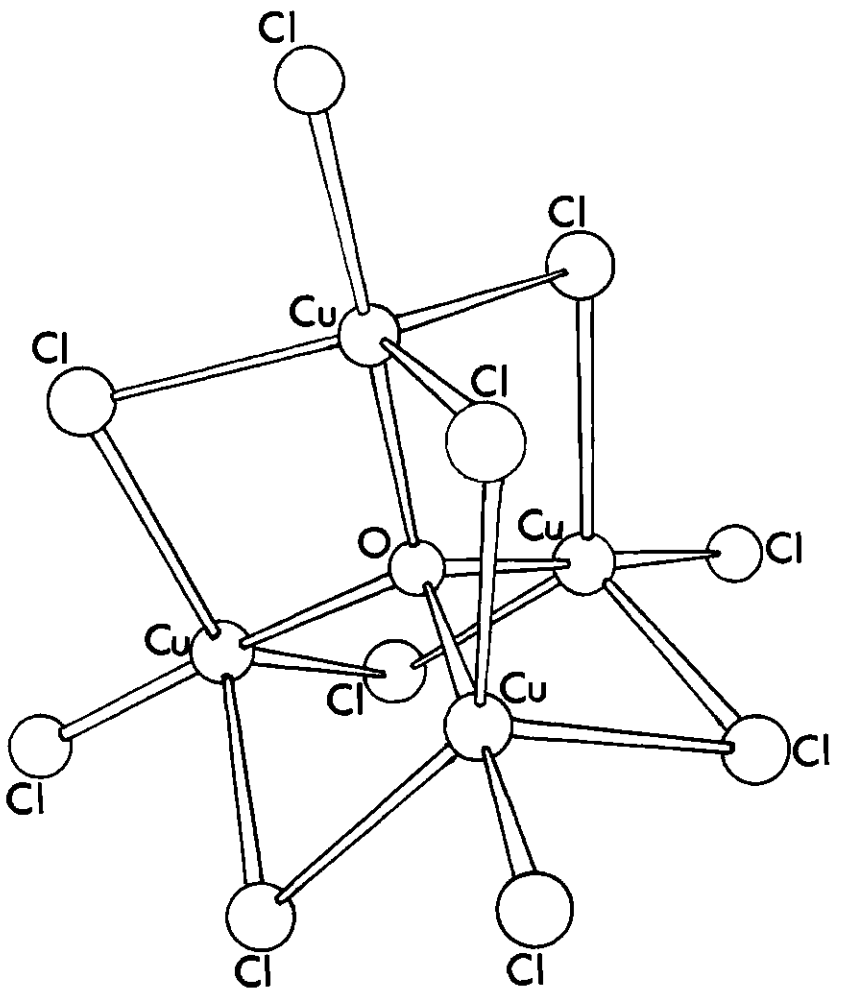


Figure 8. A Perspective Drawing of the Structure of the $Cu_4OCl_{10}^{-4}$ Anion

Table 17. Interatomic Distances and Angles Within the $Cu_4OCl_{10}^{-4}$ Anions

Atoms	Distance, A°	Atoms	Angle, degrees
Cu - O	1.945(5)	Cu - O - Cu	109.5
Cu' - O'	1.921(8)	Cu' - O' - Cu'	109.0(5)
Cu - Cu	3.18(1)		109.7(3)
Cu' - Cu'	3.14(1)	O - Cu - Cl_{ax}	180.0
Cu - Cl_{eq}	2.43(3)	O' - Cu' - $Cl_{ax'}$	177.0(7)
Cu' - Cl_{eq},(1)	2.40(2)	O - Cu - Cl_{eq}	84.5(6)
Cu' - Cl_{eq},(2)	2.38(2)	O' - Cu' - Cl_{eq},(1)	84.8(5)
	2.45(2)	O' - Cu' - Cl_{eq},(2)	85.6(5)
Cu - Cl_{ax}	2.17(2)		83.5(5)
Cu' - $Cl_{ax'}$	2.25(2)	Cl_{eq} - Cu - Cl_{eq}	119.1(2)
		Cl_{eq},(1) - Cu' - Cl_{eq},(2)	118.0(5)
			120.5(5)
		Cl_{eq},(2) - Cu' - Cl_{eq},(2)	118.9(4)
		Cl_{ax} - Cu - Cl_{eq}	95.5(8)
		$Cl_{ax'}$ - Cu' - Cl_{eq},(1)	98.2(7)
		$Cl_{ax'}$ - Cu' - Cl_{eq},(2)	93.5(7)
			94.4(7)
		Cu - Cl_{eq} - Cu	81.5(1.2)
		Cu' - Cl_{eq},(1) - Cu'	81.4(9)
		Cu' - Cl_{eq},(2) - Cu'	81.2(6)

Table 18. Interatomic Distances and Angles Within the Tetramethylammonium Cations

Atoms	Distances, A°	Atoms	Angle, degrees
N - C(1)	1.49(7)	C(1) - N - C(2)	113.8(7.2)
N - C(2)	1.31(9)	C(2) - N - C(2)	104.8(6.7)
N' - C'(1)	1.53(9)	C'(1) - N' - C'(2)	98.8(6.0)
N' - C'(2)	1.58(11)	C'(1) - N' - C'(3)	123.0(7.7)
N' - C'(3)	1.43(10)	C'(1) - N' - C'(4)	123.1(8.1)
N' - C'(4)	1.28(10)	C'(2) - N' - C'(3)	92.7(6.6)
		C'(2) - N' - C'(4)	101.8(8.4)

with the value for Copper(II) oxide, 1.95Å. Because of symmetry requirements, the octahedron of chlorides for the origin anion is undistorted; it has a Cu-Cl_{eq} distance of 2.43Å, a Cu-Cl-Cu angle of 81.5°, and a Cl_{eq}-Cu-Cl_{eq} angle of 119.1°. The octahedron of chlorides for the non-origin anion is not required to be symmetrical, but the agreement of the Cu-Cl_{eq} distances, 2.38Å - 2.45Å, the Cl_{eq}-Cu-Cl_{eq} angles, 118.0 - 120.5°, and the Cu-Cl-Cu angles, 81.4 and 81.2°, show that no appreciable distortions are present. As in previous structures of this type (10,15,17), the copper atom is displaced out of the equatorial plane (0.21Å) of the trigonal bipyramid away from the central oxygen to give Cl_{eq}-Cu-O angles of 85° for both anions. This distance is 0.23Å for $Cu_4OCl_6(TPPO)_4$ (10) and $Cu_4OCl_6(pyridine)_4$ (17). The O-Cu-Cl_{ax} arrangement is linear for the origin anion because of symmetry

requirements and is only slightly bent, 177.0°, for the non-origin anion.

Since the isotropic temperature factor of atom C(1) was somewhat high, the possibility of disorder within the tetramethylammonium group along the threefold axis was investigated but no unusual features were found in the final difference Fourier in this region.

This complex anion can be thought of as a member of the series of compounds with the general formula $Cu_4OCl_6L_4$. The basic Cu_4OCl_6 units in this structure are essentially identical to that reported when L was triphenylphosphine oxide (10). The compound with L = pyridine (17) is very similar but shows significant distortion of the chloride octahedron. The Cu-Cl_{eq} distances vary from 2.36Å to 2.49Å and the Cl_{eq}-Cu-Cl_{eq} angles vary from 108 to 138°. Since none of the other complexes with this basic formula show such distortions, it appears that intra-molecular contacts between the pyridine ring hydrogens and the chlorides of the octahedron are responsible.

The Cu-Cl_{ax} distances (2.17Å and 2.25Å) in the $Cu_4OCl_{10}^{-4}$ ions are considerably shorter than the Cu-Cl_{eq} distances (2.38Å-2.45Å). Such an effect could be attributed to π-bonding. Electron density could be donated from the copper π-orbitals to the vacant 3d orbitals of the chlorides. Such back-donation would result in the shortening of the Cu-Cl_{ax} bonds. Such an effect was also present in Bertrand's (10) $Cu_4OCl_6(TPPO)_4$ where a linear Cu-O-P arrangement and an increase in the phosphorous-oxygen stretching frequency was attributed to π-bonding between the copper and the phosphorous-oxygen system.

The coordination sphere in these polyhedral anions is very similar to that found for the $CuCl_5^{-3}$ ion (38,39). In the $CuCl_5^{-3}$ ion, the Cu-Cl_{ax} distances are considerably shorter than the Cu-Cl_{eq} distances. The Cu-Cl_{eq} distances in the $Cu_4OCl_{10}^{-4}$ (2.38Å - 2.45Å) and in the $CuCl_5^{-3}$ ion (2.39Å) are identical even though these chlorides in $Cu_4OCl_{10}^{-4}$ are bridging groups. A comparison of the Cu-Cl_{ax} distances of the $Cu_4OCl_{10}^{-4}$ ion (2.17Å - 2.25Å) with that of the $CuCl_5^{-3}$ ion (2.30Å), shows a significant shortening only in the case of the origin anion. The shorter distance for the Cu-Cl_{eq} bonds is consistent with the π-bonding argument and a shorter Cu-Cl_{ax} distance in the $Cu_4OCl_{10}^{-4}$ ions is also consistent since in the $CuCl_5^{-3}$ ion the two axial chlorides would compete for the copper electrons in the same manner that trans-carbonyl groups compete for metal electrons (and weaker bonds) in metal carbonyl complexes.

μ_4-oxo-hexa-μ-bromotetrakis{(ammine copper(II)}

A perspective drawing of the structure is shown in Figure 9 and selected bond distances and bond angles are given in Table 19. This structure is basically the same as that found for other μ_4-oxo type structures (10,15,17). As in the other μ_4-oxo type structures (10, 15,17), an oxygen atom is surrounded tetrahedrally by four copper(II) atoms. The copper atoms are bridged along the six edges of the tetrahedron by bromide atoms. The copper atoms are five coordinate with a nearly regular trigonal bipyramid being formed. The equatorial positions of the trigonal bipyramid are filled by three of the bridging bromides and the axial positions are filled by the central

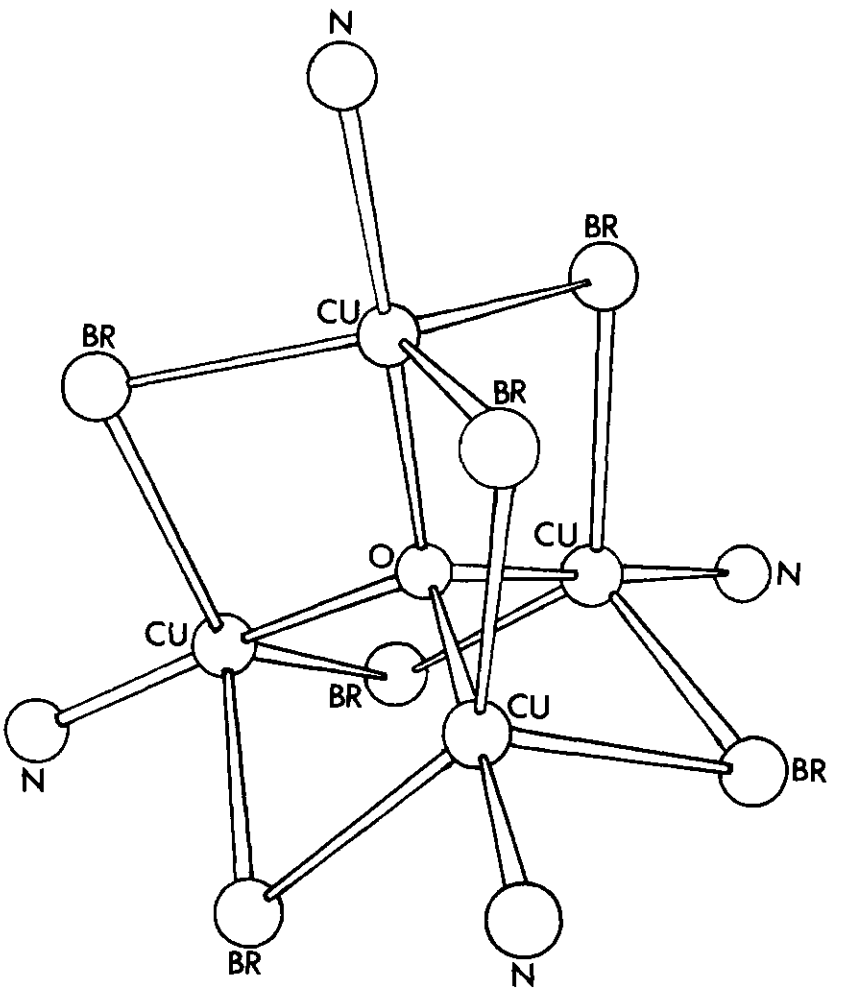


Figure 9. A Perspective Drawing of the Structure of $Cu_4OBr_6(NH_3)_4$

Table 19. Interatomic Distances and Angles for $Cu_4OBr_6(NH_3)_4$

Atoms	Distance, Å	Atoms	Angle, degrees
Cu-O	1.915(5)	Cu-O-Cu	108.7(3)
			109.9(1)
Cu-Cu	3.113(10)	O-Cu-N	179.8(1.1)
	3.135(8)	O-Cu-Br	87.2(2)
Cu-N	1.98(3)		87.5(2)
Cu-Br	2.570(7)		86.9(2)
	2.557(6)	Br-Cu-Br	118.8(2)
	2.485(6)		121.2(2)
			119.3(2)
		N-Cu-Br	93.0(1.0)
			92.5(1.1)
			92.9(1.1)
		Cu-Br-Cu	77.6(3)
			75.4(3)

oxygen and an ammonia molecule. The size of the central Cu_4O unit has not changed significantly when the bridges are bromides instead of chlorides. The Cu-O distance in this structure, 1.915Å, is the same as that found for other μ_4-oxo structures (see Table 20). The Cu-Cu distance in this structure, 3.12Å, is also in the same range found for other structures of this type.

One of the expected changes that took place when bromide bridges replaced the chloride bridges was the copper-halogen distances. The Cu-Br distances, 2.485Å-2.570Å, are longer than the corresponding $Cu\text{-}C\ell_{eq}$ distances, 2.38Å-2.45Å, in the $Cu_4OC\ell_{10}^{-4}$ ion. This change reflects the difference in size of bromine and chlorine atoms. This increase in the copper-halogen distances, with a constant Cu-Cu distance maintained, necessarily increased the size of the octahedron of halogens surrounding the central oxygen. However, this enlargement caused no distortions of the octahedron. The increase in the size of the octahedron can be seen by the decrease in the copper-halogen-copper angles. The average $Cu\text{-}C\ell_{eq}\text{-}Cu$ angle in the $Cu_4OC\ell_{10}^{-4}$ ion was 81.3° and the average Cu-Br-Cu angle in this structure is 76.5°. What actually happens when bromide replaces chloride is that the bromides are further away from the edges of the tetrahedron than were the chlorides. The enlargement of the halogen octahedron also affects the distance of the copper atom from the equatorial plane of the trigonal bipyramid. The distance is 0.12Å in this structure and is 0.11Å in $Mg_4OBr_6(C_4H_{10}O)_4$ (15). This distance is less than that found for the chloride structures (10,17) of this type (see Table 20). Another point of interest is that the overall dimensions of the Mg_4OBr_6 (15) unit and the Cu_4OBr_6 are amazingly similar (Table 20).

Although a complete structure determination was not carried out for $Cu_4OBr_6(TPPO)_4 \cdot 2CH_3NO_2$, several points can be made about the structure. The Patterson synthesis (33) yielded atomic positions for all of the atoms of the central Cu_4OBr_6 unit. These positions are not exact

Table 20. Comparison of Average Bond Distances and Bond Angles for $M_4OX_6L_4$ Structures

	M-M,Å	M-O,Å	M-L,Å	M-X,Å	Distance of Metal Out of Equatorial Plane Å
I.	3.11	1.91	1.89	2.38	0.23
II.	3.16	1.93	2.21	2.42	0.21
III.	3.09	1.90	1.96	2.41	0.23
IV.	3.12	1.92	1.98	2.54	0.12
V.	3.20	1.95	2.11	2.60	0.11
	M-O-M	X-M-X	O-M-X	M-X-M	O-M-L
I.	108.9	119.0	84.4	81.6	180.0
II.	109.4	119.1	84.6	81.4	178.5
III.	109.5	119.2	84.8	80.2	177.3
IV.	109.2	119.7	87.2	76.5	179.8
V.	109.7	119.3	87.5	75.6	179.8

I = $Cu_4OCl_6(TPPO)_4$
II = $Cu_4OCl_{10}^{-4}$
III = $Cu_4OCl_6(pyridine)_4$
IV = $Cu_4OBr_6(NH_3)_4$
V = $Mg_4OBr_6(C_4H_{10}O)_4$

since complete refinement was not attained, but they are roughly the same as those found for the Cu_4OCl_6 unit in Bertrand's structure (10). Both space groups, P23 and $P\bar{4}3m$ (34), have the same type positions for the central Cu_4OX_6 unit and it seems that both structures are made up of units occupying the same type positions. Because of the symmetry of P23, the octahedron of bromide atoms is completely symmetrical.

As were the equatorial chlorides in Bertrand's structure (10), the three bromides of the equatorial plane of the trigonal bipyramid are related by a threefold axis. Since this unit cell, a = 12.47Å, and Bertrand's unit cell, a = 12.22Å, are similar, allowing for the fact that bromides are larger than chlorides, it is very likely that the $Cu_4OBr_6(TPPO)_4$ and $Cu_4OCl_6(TPPO)_4$ units are isostructural. The phenyl rings are not required to be disordered in space group P23 as they were in $P\bar{4}3m$. The two nitromethane molecules would be required to be disordered in P23 since no twofold positions are available.

Table 20 summarizes some of the important bond distances and bond angles for some of the known structures with the general formula $M_4OX_6L_4$. Inspection of this table shows that all of the chloride structures are basically the same; some may be distorted, but average dimensions compare favorably. For this reason, it was not considered necessary to carry out structure determinations of $Cu_4OCl_6(TPPO)_4 \cdot 2CH_3NO_2$, $Cu_4OCl_6(PyO)_4$, and $[(CH_3)_4]_4Cd_4OCl_{10}$.

Single crystals of $Cu_4O(acetate)_6$ could not be obtained, but the structure is probably similar to that found for $Be_4O(acetate)_6$ (40) and $Zn_4O(acetate)_6$ (41).

Cu(EIA)

A perspective drawing of the structure is shown in Figure 10 and bond distances and bond angles are given in Table 21. The complex is tetrameric like the previously reported acetylacetone mono(o-hydroxyanil)Copper(II) complex (8). The tetrameric complex can be thought of as two dimers held together by copper-oxygen bonds. In the previous

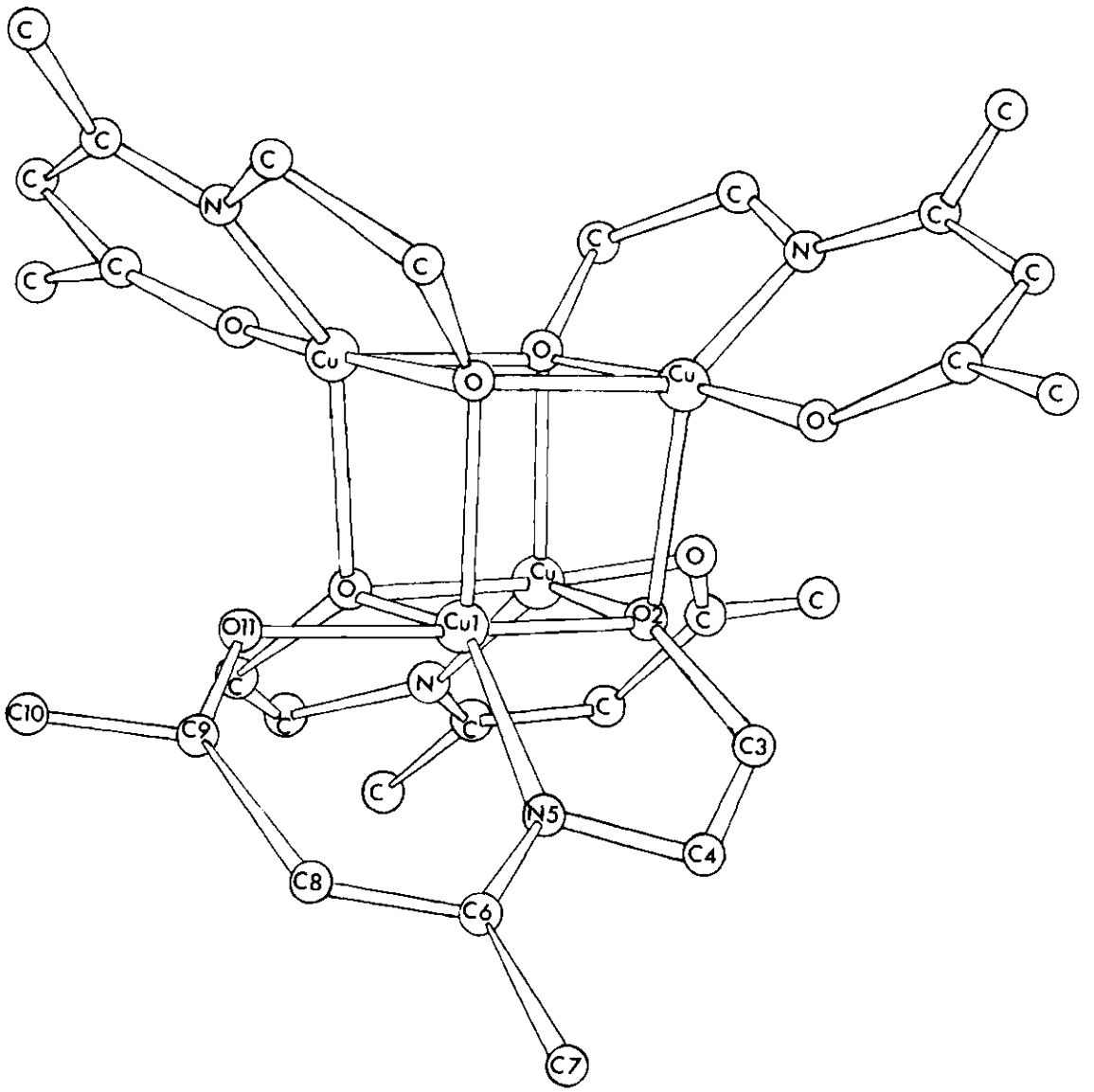


Figure 10. A Perspective Drawing of the Structure of Cu(EIA)

Table 21. Bond Distances and Bond Angles for Cu(EIA)

Atoms	Distance, Å	Atoms	Angle, degrees
Cu1-Cu1'	3.006(8)	Cu1-O2-Cu1'	97.8(8)
Cu1-Cu1"	3.259(8)	O2-Cu1-O2'	81.4(8)
Cu1-O2	1.98(2)	O2-Cu1-O2"	81.8(7)
Cu1-O2'	2.00(2)	O2'-Cu1-O2"	81.3(7)
Cu1-O2"	2.32(2)	O2-Cu1-N5	86.0(1.0)
Cu1-O11	1.91(2)	O2"-Cu1-N5	120.3(8)
Cu1-N5	1.90(2)	O2'-Cu1-N5	153.1(8)
C9-O11	1.30(4)	O2'-Cu1-O11	98.4(9)
O2-C3	1.40(3)	N5-Cu1-O11	95.0(1.1)
C4-N5	1.53(4)	Cu1-O2-C3	107.5(1.7)
N5-C6	1.30(3)	Cu1'-O2-C3	118.6(1.6)
C9-C10	1.54(5)	N5-C4-C3	106.3(2.4)
C6-C7	1.45(4)	O2-C3-C4	109.4(2.5)
C8-C9	1.39(4)	Cu1-N5-C4	110.9(1.7)
C6-C8	1.43(4)	C4-N5-C6	120.1(2.4)
C3-C4	1.51(4)	Cu1-N5-C6	128.8(2.3)
		N5-C6-C8	119.1(2.7)
		C6-C8-C9	126.7(2.9)
		C8-C9-O11	126.7(3.0)
		Cu1-O11-C9	122.9(2.1)
		O2-Cu1-O11	178.0(9)

Table 22. Equation of the Best Least-Squares Plane of the Acetylacetenate Chelate Ring (N5, C6, C7, C8, C9, C10, O11) of Cu(EIA) and the Distances (Å) of the Atoms from That Plane

$$0.499X + 0.196Y - 0.844Z = -0.329$$

N5	0.040	C9	-0.012	O2	-0.119
C6	-0.036	C10	0.041	C3	0.082
C7	0.026	O11	-0.021	C4	0.133
C8	-0.037	Cu1	-0.098		

structure (8) one dimer was displaced with respect to the other so that there were only two such Cu-O interactions per tetramer. In this complex, one dimer is rotated 90° with respect to the other so that there are four Cu-O interactions per tetramer. The Cu-Cu distance between "dimers" (3.26Å) is longer than the Cu-Cu distance within the dimer (3.01Å). As in the μ_4-oxo complexes (10,15,17), the copper atoms are arranged in a tetrahedron, but in this complex there is nothing at the center of the complex. Also, in the μ_4-oxo complexes the copper atoms were bridged above the *edges* of the tetrahedron by halogens; in this complex the copper atoms are bridged above the *faces* of the tetrahedron by oxygen atoms. The close relationship between the bonding in these two types of structures has been discussed by Kettle (42).

The coordination around the copper atom is somewhat distorted but is five-coordinate and is essentially bipyramidal with two oxygens of one chelate ligand in axial positions. The nitrogen of the same ligand and the oxygens of two other ligands of the tetramer occupy equatorial positions. As in the μ_4-oxo complexes (10,15,17), the copper is displaced out of the equatorial plane (0.23Å). The angles between the groups in the equatorial plane (81, 120 and 153°) are not indicative of square pyramidal coordination (90, 90, and 180°) nor of trigonal bipyramidal coordination (all 120°).

The four-membered ring of copper and oxygen atoms, which is not required by symmetry to be planar, is bent. The extent of bending of the ring is indicated by the dihedral angles between the two Cu-O-Cu

planes, about 14°, and between the two O-Cu-O planes, about 12°.

The tridentate ligand forms a six-membered ring (unsaturated chelate ring) and a five-membered ring (saturated chelate ring). Table 22 gives the calculated best least-squares plane of the acetylacetonate ring (unsaturated chelate ring) and the distances of the atoms from that plane. As Table 22 indicates, the unsaturated chelate ring is planar. In the saturated chelate ring, the carbon C3, bonded to the bridging oxygen is considerably out of the plane of the rest of the chelate ring.

Cu(PIA)

Figure 11 shows a perspective drawing of the structure and Table 23 gives bond distances and bond angles. The only difference between the ligand in this complex and the one in Cu(EIA) is one carbon atom in the saturated ring. This structure is dimeric and contains a central four-membered ring which, because of an inversion center at the center of the ring, is exactly planar. In addition, the coordination of each copper atom is planar as indicated by the fact that none of the coordinated atoms are out of the plane defined by the four-membered ring (see Table 24) by more than 0.03Å. The coordination around the bridging oxygen is also essentially planar with the carbon bonded to the oxygen only 0.02Å out of the plane of the four-membered ring.

In addition to the four-membered ring, there are two six-membered chelate rings consisting of copper, oxygen, nitrogen and three carbon atoms. One of these chelate rings contains carbon atoms

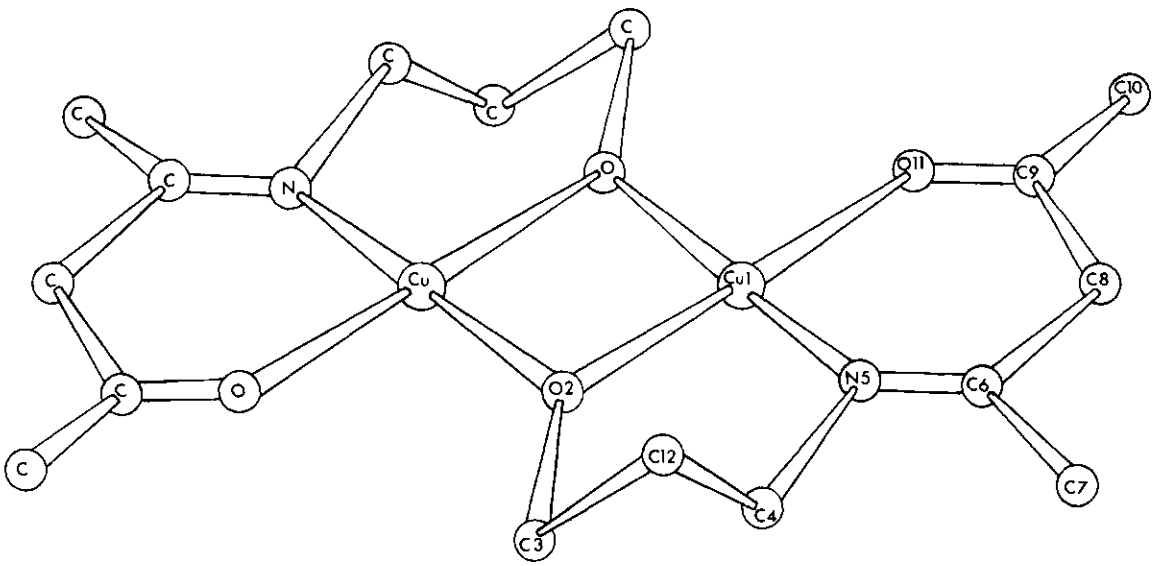


Figure 11. A Perspective Drawing of the Structure of Cu(PIA)

Table 23. Bond Distances and Bond Angles for Cu(PIA)

Atoms	Distance, Å	Atoms	Angle, degrees
Cu1-Cu1'	3.025(6)	Cu1-O2-Cu1'	106.4(6)
Cu1-O2	1.86(1)	O2-Cu1-O2'	73.6(6)
Cu1-O2'	1.92(1)	O2-Cu1-N5	99.6(6)
Cu1-O11	1.96(2)	O2'-Cu1-N5	173.1(6)
Cu1-N5	1.83(1)	O2'-Cu1-O11	91.8(6)
C9-O11	1.31(2)	N5-Cu1-O11	95.0(7)
O2-C3	1.43(2)	Cu1-O2-C3	129.4(1.2)
C4-N5	1.49(3)	Cu1'-O2-C3	124.2(1.2)
N5-C6	1.28(2)	N5-C4-C12	114.4(2.0)
C9-C10	1.52(3)	O2-C3-C12	108.2(1.6)
C6-C7	1.53(2)	C3-C12-C4	116.2(2.2)
C8-C9	1.42(3)	Cu1-N5-C4	119.6(1.4)
C6-C8	1.40(3)	C4-N5-C6	117.7(1.9)
C4-C12	1.53(3)	Cu1-N5-C6	122.7(1.5)
C3-C12	1.56(3)	N5-C6-C8	120.3(1.9)
		C6-C8-C9	125.8(1.9)
		C8-C9-O11	120.6(1.9)
		Cu1-O11-C9	129.4(1.5)

Table 24. Equations of Atomic Planes and Distances(A°) of Atoms from These Planes

(a) Equation of the Plane of the Four-Membered Ring (Cu1,O2,Cu1',O2') of Cu(PIA):

$$0.620X + 0.739Y - 0.264Z = 0.000$$

Cu1	0.000	C4	0.044	C9	-0.082
O2	0.000	N5	-0.028	C10	-0.106
Cu1'	0.000	C6	-0.120	O11	-0.006
O2'	0.000	C7	-0.230	C12	0.735
C3	0.018	C8	-0.215		

(b) Equation of the Best Least-Squares Plane of the Acetylacetonate Chelate Ring (N5,C6,C7,C8,C9,C10,O11) of Cu(PIA):

$$0.620X + 0.762Y - 0.186Z = 0.212$$

N5	0.014	C9	0.009	O2	-0.197
C6	0.019	C10	0.026	C3	-0.167
C7	0.001	O11	-0.020	C4	0.074
C8	-0.049	Cu1	-0.090	C12	0.658

from the acetylacetone (unsaturated chelate ring) and the other chelate ring contains the carbons from the aminopropanol (saturated chelate ring). The five carbon atoms of each unsaturated chelate ring are essentially coplanar (the greatest deviation of any of the five atoms from their best least-squares plane is 0.05Å) and that plane forms a dihedral angle of about 10° with the plane of the four-membered ring. Since the two unsaturated chelate rings of the dimer are related by a center of inversion, they are bent in opposite directions from the plane of the copper-oxygen ring. The carbon-carbon bond distances

within the unsaturated chelate ring do not differ by as much as their standard deviations.

The saturated chelate ring, as expected, is non-planar. As indicated above, the carbon bonded to the bridging oxygen is in the plane of the four-membered ring, the carbon bonded to the nitrogen is only slightly out of that plane (0.12Å), and the other carbon of the ring is the only atom of the entire structure that causes the dimer to deviate significantly from planarity--it is 0.74Å from the plane on the side opposite the unsaturated chelate ring of the same ligand.

Cu(SALPA)Cℓ

A perspective drawing of the structure of Cu(SALPA)Cℓ is given in Figure 12 and bond distances and bond angles for the structure are given in Table 25. This complex is dimeric as was Cu(PIA) and the copper atoms are five-coordinate as were those in Cu(EIA). Since the molecule contains a center of inversion at the center of the four-membered copper-oxygen ring, that ring is exactly planar as it was in the Cu(PIA) structure.

The Cu-Cu distance in this structure, 3.29Å, is longer than that distance found in Cu(PIA), 3.01Å, or in Cu(EIA), 3.01Å and 3.26Å. Also, the central four-membered ring in this structure is not as symmetrical as it was in Cu(PIA). The Cu-O distances within the four-membered ring for this structure, 1.78Å and 2.22Å, show a much larger difference than the two corresponding distances in Cu(PIA), 1.86Å and 1.92Å.

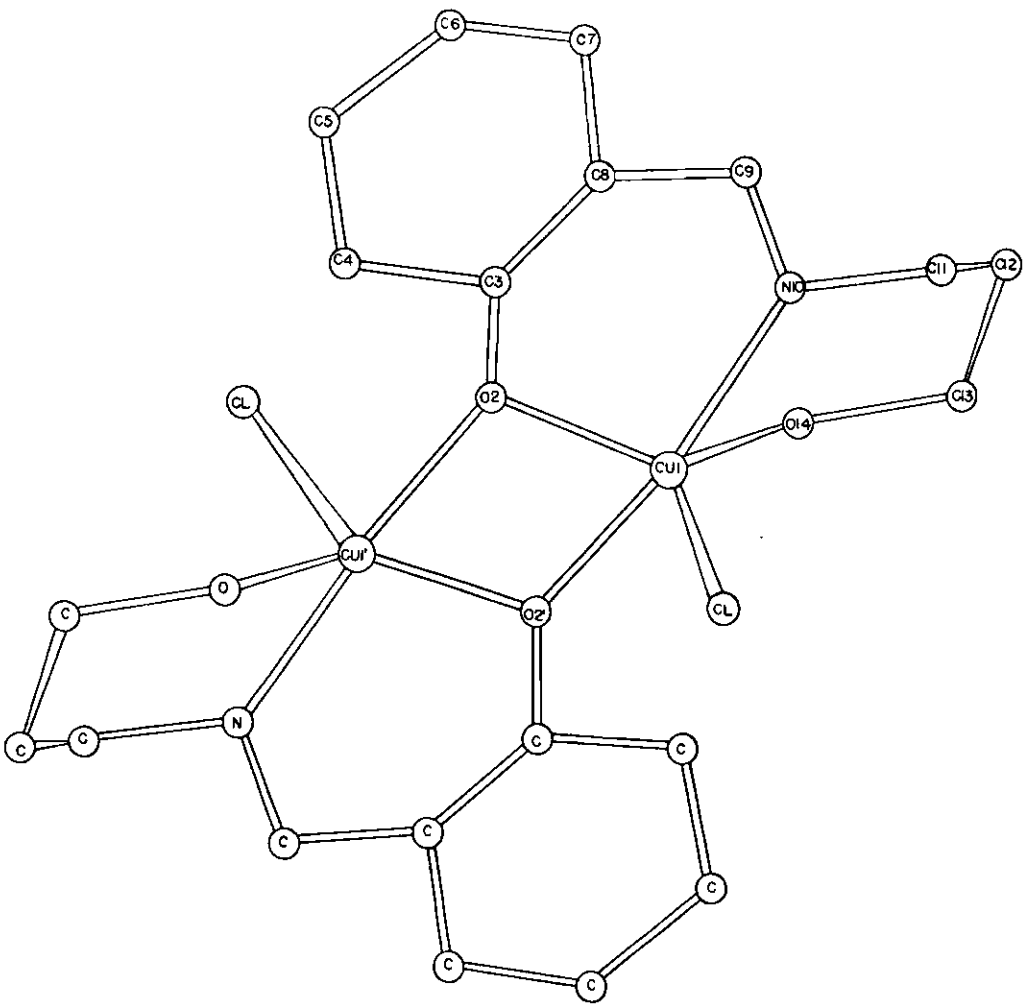


Figure 12. A Perspective Drawing of the Structure of Cu(SALPA)Cℓ

Table 25. Bond Distances and Bond Angles for Cu(SALPA)Cℓ

Atom	Distance, Å	Atoms	Angle, degrees
Cu1-Cu1'	3.294(7)	Cu1-O2-Cu1'	110.3(6)
Cu1-Cℓ	2.115(6)	O2-Cu1-O2'	69.7(6)
Cu1-O2	1.78 (1)	Cl-Cu1-O2	126.2(5)
Cu1-O2'	2.22 (1)	Cl-Cu1-O2'	98.6(4)
O2-O2'	2.31 (3)	Cl-Cu1-O14	110.1(4)
Cu1-N10	2.18 (2)	Cl-Cu1-N10	92.5(5)
Cu1-O14	2.24 (2)	O2'-Cu1-O14	99.6(6)
O2-C3	1.34 (2)	O2'-Cu1-N10	168.9(6)
C3-C4	1.39 (3)	O14-Cu1-N10	76.0(6)
C4-C5	1.38 (3)	O14-Cu1-O2	123.4(7)
C5-C6	1.53 (3)	N10-Cu1-O2	104.0(6)
C6-C7	1.34 (3)	Cu1-O2-C3	112.3(1.3)
C7-C8	1.41 (3)	Cu1'-O2-C3	137.2(1.2)
C3-C8	1.48 (3)	O2-C3-C4	98.0(1.9)
C8-C9	1.41 (3)	C4-C3-C8	133.1(2.0)
C9-N10	1.19 (2)	C8-C3-O2	128.9(1.9)
N10-C11	1.54 (3)	C3-C4-C5	100.6(2.1)
C11-C12	1.60 (3)	C4-C5-C6	127.6(2.1)
C12-C13	1.63 (3)	C5-C6-C7	129.8(2.2)
C13-O14	1.53 (3)	C6-C7-C8	104.4(2.0)

Table 25. (Continued)

Atoms	Angle, degrees
C7-C8-C3	123.9(1.9)
C7-C8-C9	97.1(1.8)
C3-C8-C9	139.0(1.8)
C8-C9-N10	110.2(2.0)
C9-N10-Cu1	125.4(1.6)
C11-N10-Cu1	130.7(1.7)
C9-N10-C11	103.9(1.8)
N10-C11-C12	114.1(1.7)
C11-C12-C13	105.0(1.8)

The coordination of the copper can be thought of as being bipyramidal. The angles within the equatorial plane (126°, 110° and 123°) are not too far from those of a regular trigonal bipyramid (all 120°). The phenolic oxygen, the oxygen of the aminopropanol of one ligand, and the chlorine occupy the equatorial positions; the nitrogen and the phenolic oxygen of the other ligand occupy the axial positions. The N10-02' angle of 169° shows the amount of bending of these axial groups from the 180° of a regular trigonal bipyramid. If the coordination is assumed to be distorted trigonal bipyramidal, the copper is only 0.06Å out of the equatorial plane, away from 02'.

As in the Cu(PIA) structure, the coordination of the bridging oxygen is essentially planar. The carbon bonded to the bridging oxygen, C3, is only 0.08Å out of the plane defined by the central four-membered ring.

Table 26 gives the calculated best least-squares planes for the central four-membered ring and the distances of atoms from that plane. A similar plane is also given for the benzene ring.

Cobalt Trimer

A perspective drawing of the structure is given in Figure 13 and selected bond distances and bond angles are given in Table 27. It has been found that this compound has a trinuclear structure. Hydrated salts of similar compounds have been prepared and have been assumed (43) to have a trinuclear structure with two tris-(2-aminoethoxido)cobalt(III) groups sharing triangular octahedral faces of oxygen atoms with a central octahedrally coordinated cobalt(II) atom.

Table 26. Calculated Best Least-Squares Planes and Distances of Atoms from Planes

Atoms Defining Plane: Cul, Cul', O2 and O2'.
Equation of Plane: -0.471X - 0.882y + 0.012Z = 0.

Atom	Distance from Plane, Å
Cul	0.00
Cul'	0.00
O2	0.00
O2'	0.00
C1	-1.70
C3	0.08
C4	-0.13
C5	-0.04
C6	0.26
C7	0.47
C8	0.35
C9	0.54
N10	0.35
C11	0.59
C12	2.00
C13	2.06
O14	1.87

Atoms Defining Plane: C3, C4, C5, C6, C7 and C8.
Equation of Plane: 0.360X + 0.922y + 0.142Z - 0.138 = 0.

Atom	Distance from Plane, Å
C3	-0.005
C4	-0.007
C5	-0.009
C6	-0.001
C7	-0.006
C8	0.008
C9	0.054
N10	0.201

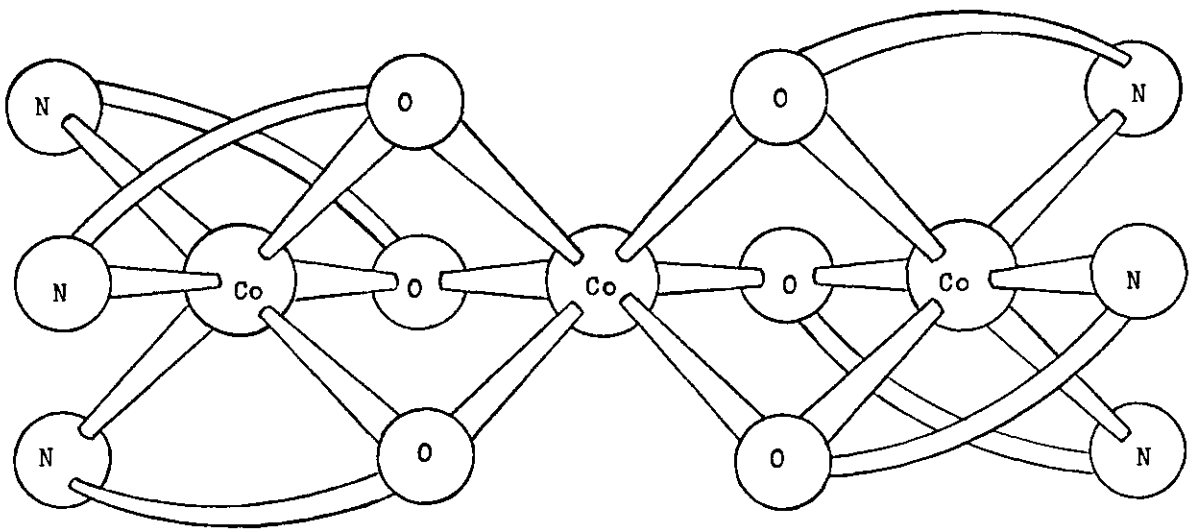


Figure 13. A Perspective Drawing of the Structure of the Cobalt Trimer

Table 27. Selected Bond Distances and Bond Angles for Cobalt Trimer

Atoms	Distance, Å	Atoms	Angle, Degrees
Co1-Co2	2.597(5)	O3-Co1-O2	
Co1-O1	2.005(3)	O3-Co1-O2	78.9(5)
Co2-O1	1.885(7)	O3-Co1-O1	78.7(5)
Co1-O2	2.104(2)	O1-Co1-O2	79.2(1)
Co2-O2	1.975(5)	O3-Co1-O1'	86.9(5)
O1-O2	2.621(4)	O2-Co1-O2'	83.0(1)
Co1-O3	2.068(18)	O1-Co1-O3'	86.9(5)
Co2-O3	1.926(19)	N1-Co2-O2	172.1(7)
O1-O3	2.582(19)	N1-Co2-N3	92.7(1.0)
O2-O3	2.648(18)	N1-Co2-O3	86.9(8)
Co2-N1	1.883(18)	N1-Co2-O1	96.2(6)
Co2-N2	1.994(20)	N1-Co2-N2	95.1(8)
Co2-N3	2.016(29)	O3-Co2-N2	172.5(9)
N2-C11	1.36(3)	O3-Co2-N3	92.1(1.0)
C11-C12	1.54(4)	O3-Co2-O2	85.5(6)
C12-O1	1.65(3)	O3-Co2-O1	85.3(6)
N1-C21	1.48(3)	N3-Co2-O1	170.6(8)
C21-C22	1.53(3)	N3-Co2-O2	85.3(9)
C22-O3	1.39(4)	N3-Co2-N2	95.0(1.0)
N3-C31	1.55(4)	O2-Co2-N2	92.7(6)
C31-C32	1.51(4)	Co2-N1-C21	110.3(1.4)
C32-O2	1.38(3)	N1-C21-C22	99.1(2.0)
CA1-CA2	1.48(4)	C21-C22-O3	110.3(2.2)
CA2-O1A	1.25(4)	C22-O3-Co1	122.7(1.6)
CA2-O1AB	1.38(4)	Co2-N2-C11	113.1(1.5)
CA2-O2A	1.38(6)	N2-C11-C12	103.4(2.2)
CA2-O2AB	1.17(6)	C11-C12-O1	104.8(1.9)
O2-O2'	2.79(1)	C12-O1-Co1	110.8(1.0)
O1-O3'	2.80(2)	Co2-N3-C31	103.7(1.7)
		C31-C32-O2	106.1(2.7)
		C32-O2-Co1	120.5(1.5)
		O3-Co1-O3'	140.8(1.0)
		O3-Co1-O2	134.1(5)
		O1-Co1-O1'	136.2(1)
		O1-Co1-O2'	138.2(1)
		O2-Co1-O3'	134.1(5)
		O2-Co1-O1'	138.2(1)
		O3-O1-O2	61.2(4)
		O1-O2-O3	58.7(4)
		O2-O3-O1	60.1(4)

Analogous trinuclear complexes, $[M(Co(chelate)_3)_2]^{+m}$, with 2-aminoethanethiolate as the chelate ligand and with cobalt(III), zinc(II) and nickel(II) as the central metal, M, have been studied and a trinuclear structure with each atom octahedrally coordinated has been proposed for these complexes (44,45).

The way in which the chelate rings are placed about the metal atoms, namely, three rings closed around each terminal cobalt(III) atom and none around the central cobalt(II) atom is not too surprising since the amino groups cannot act as bridging groups. The surprising part of the structure is the coordination of the central cobalt(II) atom. The coordination of the terminal cobalt(III) atoms is essentially octahedral with three Co-N distances of 1.88, 1.99 and 2.02Å and three Co-O distances of 1.89, 1.93 and 1.98Å while the coordination of the central cobalt(II) atom is an almost perfect trigonal prism. The Co-O distances are 2.01, 2.07 and 2.10Å. The triangular faces of the trigonal prism are almost perfect equilateral triangles with O-O distances of 2.58, 2.62 and 2.65Å and angles of 58.7, 60.1 and 61.2°. Between the triangular faces there are two O-O distances of 2.80 and one of 2.79Å. The best least-squares plane for the group of four oxygens comprising each rectangular face of the trigonal prism was calculated, the distance of each atom from the plane was calculated and the dihedral angle between each pair of adjacent faces was calculated; no atom was more than 0.05Å out of the plane of its face and the dihedral angles between the faces were 121.5° for one pair and 119.1° for the other two pair.

Since a twofold axis relates the two terminal cobalt(III) atoms, each has the same optical configuration and thus, the complex should be optically active. Construction of models of the structure found and of the postulated structure with octahedral coordination about the central cobalt(II) indicates the hydrogen atoms of the methylene groups adjacent to the oxygens may be responsible for the unusual coordination. Hydrogens of the two chelates appear to approach to less than the sum of their Van der Waal's radii in the octahedral complex but are less crowded in the trigonal prismatic complex. On the basis of models, octahedral coordination would give less crowding of the hydrogens in the inactive complex in which the cobalt(II) atom is coordinated to one Λ and one Δ tris chelate.

The Co-Co distance in this structure, 2.60Å, is shorter than that found for other first row transition metal trinuclear structures. Cotton (46) found a Co-Co distance of 2.92Å for $Co_3(DEPAM)_6$, where DEPAM is the diethoxyphosphonylacetylmethane anion and the Ni-Ni distance is 2.89Å in the trinuclear nickel acetylacetonate. As found for this structure, Cotton's $Co_3(DEPAM)_6$ structure had three chelate rings around each terminal cobalt atom and none around the central cobalt. However, one would expect a longer Co-Co distance in $Co_3(DEPAM)_6$ since there would be more repulsion between the methyl groups on the DEPAM ligands than there was for the methylene hydrogens on the 2-amino-ethoxido ligands. This would also be true for the methyl groups on the acetylacetonate ligands of nickel acetylacetonate. Metal-metal bonding cannot be ruled out for this structure. The magnetic moment per trimer,

4.05 Bohr magnetons, is reasonable for three unpaired electrons. The two cobalt(III) atoms would not affect this value even if metal-metal bonding were present.

This complex represents the first example of a trigonal prismatic complex with a coordination sphere of oxygen atoms. The only other discrete complexes reported to have trigonal prismatic coordination have been with the dithiolate ligand (47). Since this complex was reported the structure of a trigonal prismatic complex, cis, cis-1, 3,5-tris(pyridine-2-carboxaldimino)cyclohexane zinc(II) ion, with a coordination sphere of nitrogen atoms was reported by Wentworth, et al. (48).

Correlations Between Magnetic Properties and Structure

The common feature of the five copper(II) structures, $Cu_4OCl_{10}^{-4}$, $Cu_4OBr_6(NH_3)_4$, Cu(PIA), Cu(EIA) and Cu(SALPA)Cl, is that they all contain copper(II) atoms bridged by oxygen atoms. The type of bridge varies from a four-coordinate oxygen in the μ_4-oxo complexes and in Cu(EIA) to a planar three-coordinate oxygen in Cu(PIA) and Cu(SALPA)Cl. Usually when copper(II) atoms are bridged by oxygen atoms, magnetic exchange occurs (1), and results in a lowering of the room temperature magnetic moment. However, as Table 16 shows, there is a wide range in the room temperature magnetic moments for these compounds--the magnetic moments vary from normal for Cu(EIA) to almost diamagnetic for Cu(PIA).

Although the formulas of Cu(PIA) and Cu(EIA) differ by only one carbon atom, the room temperature magnetic moments, 0.41 and 1.87 Bohr

magnetons, respectively, are markedly different. As indicated above, a subnormal magnetic moment, as that of Cu(PIA), is characteristic of a large number of oxygen-bridged copper(II) complexes (1). The moment of Cu(EIA), although normal for an isolated copper(II) ion, is unusual for an oxygen-bridged complex. Other previously reported examples with normal magnetic moments are dimers of bis chelates (49), as the bis 8-hydroxyquinoline chelate, the dimeric complex of N,N'-ethylene-bis(salicylindeneiminato) (50) and the μ_4-oxo complexes (10,17). Because of the large difference in room temperature magnetic moments, a comparison of the structures of Cu(PIA) and Cu(EIA) should provide additional evidence as to the mechanism of the spin-exchange interaction in oxygen-bridged complexes.

The principal difference in the two structures is the coordination of the bridging oxygens--in Cu(PIA) coordination about oxygen is planar while in Cu(EIA) coordination around oxygen is tetrahedral; the difference can be understood in terms of the chelate rings formed. In order for the coordination around a bridging oxygen to be planar (sp^2 hybridization), the Cu1-O2-C3 angle must be at least 120° (since the Cu1-O2-Cu1' angle is considerably less than 120°, the two Cu-O-C angles for each oxygen must average more than 120° to maintain planarity). In the case of Cu(PIA), it is possible to have Cu-O-C angles of 129° and 124° *and* square-planar coordination around copper without any steric strain; however, the same arrangement in Cu(EIA), because of the smaller chelate ring, would be extremely strained. The strain can be relieved to some extent by a change to sp^3 hybridization of the oxygen orbitals, thus decreasing the Cu-O-C angle within the chelate

ring; this angle is 108° in Cu(EIA).

With the change in hybridization of the oxygen, the ethanolimine ligand makes it impossible to have a planar four-membered metal-oxygen ring *and* square-planar coordination of the metal; in Cu(EIA), the four-membered ring is slightly bent (the two Cu-O-Cu planes show a dihedral angle of 14°) and the coppers are five-coordinate. In the corresponding nickel complex (51), square-planar coordination of the metal is maintained but the four-membered ring shows much greater bending (the two Ni-O-Ni planes show a dihedral angle of 40°).

In the case of the planar arrangement, three of the four outer orbitals of each bridging oxygen (2s, $2p_x$, and $2p_y$) are used for σ-bonding and the fourth orbital ($2p_z$) is available for π-bonding with the copper d_{xz}, d_{yz} orbitals; in the case of the non-planar tetramer, the fourth orbital does not have π-symmetry and it enters into σ-bonding, forming the cubane-type structure.

It seems significant that for all of the oxygen-bridged copper(II) complexes with normal magnetic moments at room temperature structure studies (9,10,17,49,50) have indicated tetrahedral hybridization of the outer orbitals of oxygen and π-bonding is not possible.

Although the oxygen $2p_z$ orbital and the copper d_{xz},d_{yz} orbitals of Cu(PIA) have the correct symmetry for forming π-type molecular orbitals (52), the assumption that dπ-pπ overlap would raise the π^* orbital above the σ^* $d_{x^2-y^2}$ orbital--a condition necessary if the π-interaction is to account for the difference in magnetic properties of these two compounds may be questioned. However, other possible

explanations of the magnetic properties may be eliminated by a comparison of the structures. Super-exchange involving the Cu $d_{x^2-y^2}$ orbitals (σ-overlap) has been suggested; although the Cu-O bonds within the four-membered rings of the two structures differ by approximately 0.10A°, it seems unlikely that such a small difference could lead to the dramatic difference in magnetic properties; furthermore, the Cu-O distances in $CuCl_2(PyO)$ (7), which has a low magnetic moment, are longer than those in Cu(EIA). Metal-metal σ-bonding has been suggested for some vanadyl complexes (53) of Schiff's bases and is also a possibility in the copper compounds; the fact that the Cu-Cu distances in Cu(EIA) and Cu(PIA) are almost identical rules out that possibility. Metal-metal π-bonding (through d_{z^2} orbitals) can be ruled out on the same basis.

The only possibility remaining is a π-interaction involving the oxygen pπ orbitals and the copper dπ orbitals as in $Ru_2OCl_{10}^{-4}$. The six orbitals in C_i symmetry can be combined to form three molecular orbitals of A_g symmetry and three molecular orbitals of A_u symmetry. One molecular orbital of A_g symmetry and one of A_u symmetry will be strongly bonding, one orbital of each symmetry will be anti-bonding, and the remaining two orbitals (on the metal ions) will be essentially non-bonding. Of the ten electrons available, eight will fill the bonding and non-bonding orbitals and there will be two electrons for the pair of anti-bonding orbitals. The two anti-bonding orbitals are not degenerate, and the energy difference would be expected to be small and, thus, would give rise to a singlet ground state and a low-lying triplet state. Furthermore, since the copper dπ orbitals also overlap

with the π-system of the chelate ring and since the different symmetries of the two anti-bonding orbitals cause them to interact differently with the chelate π-system, the energy difference would be affected by changes in the chelate π-system; in the case of the pyridine-N-oxide complexes, the interaction of the oxygen π-orbital with the pyridine π-system would also affect the energy difference. In studies of copper complexes of substituted pyridine-N-oxides (54) and in studies of both copper (55) and vanadyl (53) complexes of Schiff's bases formed from substituted salicylaldehydes and substituted o-aminophenols, some correlation between J (the energy difference between the pair of anti-bonding orbitals) and the resonance substituent constants has been observed.

The same explanation has been given previously (52) (D_{2h} symmetry was assumed) but omission of the pair of d_{xy} orbitals from the final molecular orbital diagram resulted in an incorrect filling of orbitals; in D_{2h} symmetry, the highest filled level should be the b_{1u} anti-bonding orbital derived from the d_{xz},d_{yz} orbitals of the coppers.

The low magnetic moments of the vanadyl complexes were previously explained by assuming a direct overlap of d_{xy} orbitals; however, if the above π-bonding explanation is correct, the lowest lying d-orbital would be one of the non-bonding π-orbitals. The pair of nonbonding orbitals is not degenerate and the interaction of the orbitals with chelate π-orbitals of different symmetries would lead to a slight energy difference consistent with the observed values of J.

It should be pointed out that the oxygen-bridged copper(II) complexes which have normal moments at room temperature may exhibit spin-exchange at lower temperatures; such effects have been observed in the μ_4-oxo complexes (56) and in Cu(EIA) (57). Although spin-exchange through a pi-mechanism is not possible for such complexes, other mechanisms (which give rise to smaller splittings) are still possible.

Although the mechanism of magnetic interaction in copper(II) oxygen-bridged complexes seems to be answered by the comparison of the structures of Cu(PIA) and Cu(EIA), there is still the possibility that the difference in magnetic properties may be due to either the difference in coordination of the copper atoms or the difference in coordination of the bridging oxygen atoms.

Table 28 summarizes the relationships between the molecular structures and magnetic moments for the μ_4-oxo complexes, Cu(EIA) and Cu(PIA). This table shows that the differences in the magnetic properties of these complexes could be due to a difference in the coordination of the copper atoms *or* a difference in the coordination of the bridging oxygen atoms. A complex with four-coordinate, square planar copper atoms *and* four-coordinate tetrahedral bridging oxygen atoms *or* a complex with five-coordinate trigonal bipyramidal copper atoms *and* three-coordinate planar bridging oxygen atoms would provide the necessary information to clarify this point. This question was not answered by the structure determination of the copper(II) O-hydroxyanil complex (8), since the complex contained both four and five-coordinate copper

Table 28. Relationships Between Molecular Structures and Magnetic Moments

Type of Structure	Coordination of Copper Atom	Coordination of Bridging Oxygen Atom	Magnetic Moments, B.M.
μ_4-oxo complexes	five-coordinate trigonal bipyramidal	four-coordinate tetrahedral	2.0-2.2
Cu(EIA)	five-coordinate trigonal bipyramidal	four-coordinate tetrahedral	1.87
Cu(PIA)	four-coordinate square planar	three-coordinate planar	0.41
Cu(O-hydroxyanil)	four-coordinate square planar and five-coordinate trigonal bipyramidal	three-coordinate planar and four-coordinate tetrahedral	1.37
$Cu(PyO)C\ell_2$	questionable	three-coordinate planar	0.85

atoms and three- and four-coordinate bridging oxygen atoms. The structure of Cu(pyridine-N-oxide)$C\ell_2$(7) was first reported to contain four-coordinate copper atoms and three-coordinate bridging oxygen atoms, but more recently it has been shown (58) that there is a chlorine atom from a neighborhing dimer 2.84Å from the copper atom. This chlorine would affect the coordination around copper but it is questionable whether it should be included in the coordination sphere of copper. The questions raised by the data in Table 28 were answered by the structure determination of Cu(SALPA)Cℓ. As mentioned above, this structure contains features common to both Cu(PIA) and Cu(EIA).

The complex is dimeric as Cu(PIA) and the copper is five-coordinate as in Cu(EIA). The copper atom in Cu(SALPA)Cℓ has a coordination that closely approximates a trigonal bipyramid. The angles within the equatorial plane (110, 123 and 126°) are not very far from those of a regular trigonal bipyramid (all 120°). The N10-Cu-O2' angle of 169° is not very far from "ideal" angle of 180° for a trigonal bipyramid. The coordination of the copper atom in Cu(EIA) was neither trigonal bipyramidal or square pyramidal; but if one assumes the coordination to be trigonal bipyramidal for the sake of discussion, the angles within the equatorial plane (81, 120 and 153°) show the trigonal bipyramid to be quite distorted in that plane. However, the "axial" angle of 178° is quite close to the predicted value of 180°. It seems unlikely that the difference in the degree of distortion of the trigonal bipyramids would account for the difference in the room temperature magnetic moments of Cu(EIA) and Cu(SALPA)Cℓ. Figure 14 compares the bond distances within the coordination spheres of Cu(EIA) and Cu(SALPA)Cℓ.

The possibility that metal-metal bonding is significant in the magnetic exchange process in these complexes is further eliminated by the fact that the Cu-Cu distance (3.29Å) in Cu(SALPA)Cℓ is longer than any of the Cu-Cu distances within the tetrameric Cu(EIA), 3.01 and 3.26Å. If metal-metal bonding had been important, it seems likely that there would have been more interaction between the coppers in Cu(EIA) where the copper atoms are closer together.

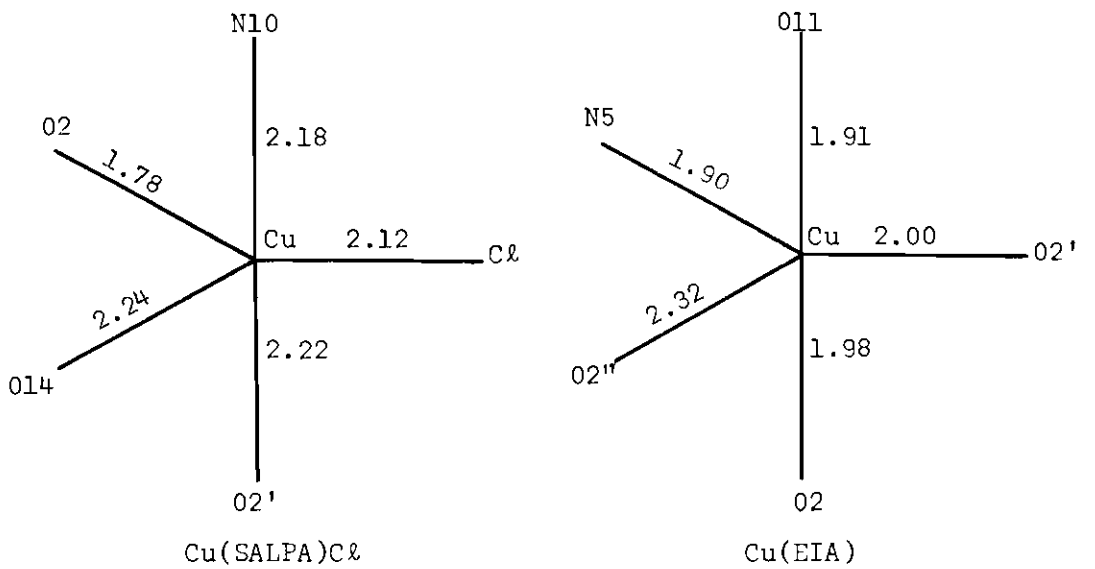


Figure 14. Comparison of Trigonal Bipyramid Bond Distances for Cu(EIA) and Cu(SALPA)Cℓ

With the possibility of metal-metal bonding being further ruled out and having shown that a difference in coordination number for the copper is not significant, the postulation that the spin-exchange process is through a π-system within the central four-membered ring is further substantiated. Indeed, the planarity of the coordination around the bridging oxygens is the feature common to both structures, Cu(PIA) and Cu(SALPA)Cℓ, that show a subnormal room temperature magnetic moment.

Spectra

Plymale (36) has shown that a copper(II) atom in D_{3h} symmetry with five equivalent ligands should show two bands in the electronic spectrum. The low-energy transition, $A' \rightarrow E'$, is electronically allowed and the high-energy transition, $A' \rightarrow E''$, is vibronically allowed. The

trigonal bipyramidal $CuCl_5^{-3}$ ion shows two absorption bands (12,13) at 8.2kK and 10.4kK. Bertrand (10) reported the absorption spectrum of $Cu_4OCl_6(TPPO)_4$ to show two absorption bands at 9.9kK and 11.2kK. Thus, it is probably reasonable to assume D_{3h} symmetry for all of the μ_4-oxo compounds reported here. However, inspection of Plymale's (36) correlation diagram for a d^9 configuration in D_{3h} symmetry shows two points. First, as the field strength increases around the copper atom, the energy of the absorption bands should increase. This is what Bertrand found for the spectrum of $Cu_4OCl_6(TPPO)_4$. The two axial positions of the trigonal bipyramid are oxygens in $Cu_4OCl_6(TPPO)_4$ instead of chlorines as in $CuCl_5^{-3}$. Second, as the field strength increases there should be a greater separation between the two predicted bands. However, Bertrand did not find this to be true. There was a smaller separation between the bands in $Cu_4OCl_6(TPPO)_4$ than there was in $CuCl_5^{-3}$. This probably arises from the fact that Plymale's correlation diagram assumes five equivalent groups around the copper. In Bertrand's complex this is not the case. In Bertrand's compound the axial ligands were oxygens and the equatorial ligands were chlorides (as in $CuCl_5^{-3}$). Thus, one might expect the major difference in the spectra would be a shift of the absorption to higher energy, which is the case. This is reasonable since the d_{z^2} orbital on the trigonal bipyramid corresponds to the A' state of the correlation diagram and this orbital is the only one that feels any appreciable change when oxygens are replaced for chlorides. There would probably be some change in the separation of the two E states but this change is less predictable.

This means that for copper(II) complexes not in a uniform ligand field Plymale's correlation diagram can only be used qualitatively.

The absorption spectrum of $Cu_4OBr_6(TPPO)_4$ shows one large absorption bond centered at 11.2kK and a smaller band at 15.6kK. The low-energy band is probably the same band seen in other μ_4-oxo complexes. For this compound, the two theoretical bands have merged to form one fairly broad band. As Bock (16) found for $Cu_4OC\ell_6(pyridine)_4$ and $Cu_4OBr_6(pyridine)_4$, the absorption spectra of the $Cu_4OBr_6(TPPO)_4$ and $Cu_4OC\ell_6(TPPO)_4$ do not differ very much. The band at 15.6 kK is attributed to some decomposition product. This is reasonable since dilute solutions, about 10^{-4} moles/liter, were used in determining the spectrum, and Bock (16) did not find any band at this energy in any of his complexes. The absorption spectrum of $Cu_4OC\ell_6$(pyridine-N-oxide)$_4$ is very similar to that found for $Cu_4OC\ell_6(pyridine)_4$. The spectrum of the ionic $Cu_4OC\ell_{10}^{-4}$ is also very similar to those reported for other μ_4-oxo complexes.

If the copper atoms in Cu(EIA) and Cu(SALPA)Cℓ are assumed to have approximate D_{3h} symmetry, the observed absorption spectra can be related to the spectra of the previously reported trigonal bipyramidal complexes. Cu(EIA) shows one broad absorption bond at 15.5 kK. There are four oxygens and one nitrogen surrounding the copper and one would predict that the absorption bonds for this complex would appear at higher energies than those of $CuC\ell_5^{-3}$ and the μ_4-oxo complexes. This is indeed what the observed spectrum of Cu(EIA) shows. A more quantitative analysis of the spectrum of this complex would be very

difficult since the field strength is not symmetrical and the true symmetry is much lower than D_{3h}.

Since Cu(SALPA)Cℓ has two oxygens and one chlorine in the equatorial plane, one might expect the absorption spectrum to show maxima between the maximum of μ_4-oxo complexes with three halogens in the equatorial plane and the maximum of Cu(EIA) with two oxygens and one nitrogen in the equatorial plane absorbed. The observed spectrum of Cu(SALPA)Cℓ shows a band at 14.3 kK which is between the absorption maxima of the μ_4-oxo complexes and Cu(EIA). A large charge transfer band also is present at higher energy.

Since the copper atom in Cu(PIA) is square planar, its absorption spectrum cannot be meaningfully compared to the previous spectra. Cu(PIA) shows an absorption bond at 17.9 kK and a large charge transfer band at higher energy. Theoretically square planar copper(II) complexes should show three absorption bonds (58), but the absorption spectra of Cu(PIA), copper(II) acetylacetonate (59) and other square planar copper(II) complexes do not show all three of these bands. The absorption spectra for copper(II) acetylacetonate has been resolved into its three components by computer methods by Schievelbein (58). No attempt was made to resolve the spectra of Cu(PIA) into the separate components.

CHAPTER IV

CONCLUSIONS

Before this work began there were several types of oxygen-bridged transition metal complexes known (1), but there had been no systematic attempt to correlate their solid state structures with their magnetic properties. Bertrand (9,10) had just prepared and completed the structure (9,10) of the first transition metal μ_4-oxo complex. In this structure the central oxygen was tetrahedrally coordinated and the complex had a magnetic moment which was normal for a trigonal bipyramidal copper(II), but unusual for an oxygen-bridged copper(II) complex. This thesis has reported the preparation of several new μ_4-oxo complexes and the complete structures of two of these complexes. The $Cu_4OCl_{10}^{-4}$ anion and $Cu_4OBr_6(NH_3)_4$ have structures very similar to that of Bertrand's $Cu_4OCl_6(TPPO)_4$. The octahedron of halogens in the bromo complex was significantly larger than that in the known chloro complexes of this type, but the tetrahedron of copper(II) atoms remained the same in all of the complexes. A partial structure of $Cu_4OBr_6(TPPO)_4 \cdot 2CH_3NO_2$ indicated that the structure is essentially the same as that of $Cu_4OCl_6(TPPO)_4$. The preparation of the μ_4-oxo complexes $Cu_4O(acetate)_6$ and $Cd_4OCl_{10}^{-4}$ are also reported. After this work began, several other μ_4-oxo complexes of transition metal ions were reported, such as $Cu_4OCl_6(pyridine)_4$ (17) and $Co_4O(pivalate)6$ (60). A comparison of the structures of several

μ_4-oxo complexes suggests that any distortions of the octahedron of halogens were probably due to intramolecular interactions instead of intermolecular interactions as Dunitz (17) suggested for $Cu_4OCl_6(pyridine)_4$.

The two complexes with subnormal magnetic moments, Cu(PIA) and Cu(SALPA)Cl, have planar coordination for the bridging oxygens, a feature consistent with π-bonding. The complexes with normal magnetic moments, Cu(EIA) and the μ_4-oxo complexes, have tetrahedral coordination for the bridging oxygen(s); no π-system can be present since all of the outer orbitals on the bridging oxygen(s) were used in the σ-bonding. The effect of a σ-interaction on the magnetic exchange is unknown but seems to be minimal as the magnetic moments of Cu(EIA) and the μ_4-oxo compounds indicate. The effect of metal-metal bonding on the magnetic exchange also seems to be minimal since the Cu-Cu distances are the same in Cu(PIA) and Cu(EIA) even though the magnetic moments differ significantly; the Cu-Cu distance in Cu(SALPA)Cl is longer than in Cu(EIA), yet the magnetic moment of Cu(SALPA)Cl is subnormal while that of Cu(EIA) is normal. On the basis of these results, the most effective mechanism for magnetic exchange in these complexes is a π-interaction.

Because of the uniqueness of the structures of some of these complexes and because of the unusual magnetic properties of these complexes, there are several parts of this work that merit further study, some of which are already in progress. Dunn (61) proposed to investigate the spectral properties of the $Cu_4OCl_{10}^{-4}$ anion in more

detail since this complex provides a good example of a copper(II) atom with trigonal bipyramidal coordination. Martin and Ginsberg (57) have studied the temperature-dependent magnetic properties of $Cu_4OCl_6(TPPO)_4$ and plan a similar study for the other μ_4-oxo complexes and for Cu(EIA). They also plan to study the electron spin resonance spectra of these complexes. Hatfield (62) is currently investigating the temperature-dependent magnetic properties of Cu(PIA).

It is interesting and important to note that the explanation given for the magnetic exchange in these copper(II) complexes is the same as that given for $Ru_2OCl_{10}^{-4}$ (4), that is, $d\pi$-$p\pi$-$d\pi$ bonding between the bridging oxygen(s) and the metal atoms. Figgis, et al. (6) suggested that the magnetic interaction in the basic acetates of Cr(III) and Fe(III) occurred through the M-O-M system at the bridging oxygen but did not elaborate on this point. If the d_{xz} or d_{yz} orbital on each metal atom overlapped with the p_z orbital on the central oxygen and formed a 4-centered delocalized π system within the M_3O unit, a reasonable pathway would be provided for magnetic exchange in these complexes.

It is noteworthy to point out that the explanation of the magnetic properties of these complexes in terms of a delocalized π system is the same as that suggested for the subnormal magnetic moment of copper(II) formate tetrahydrate (1). This suggests that this explanation might be general for all degrees of polymerization, from dimers to extended-type structures, for these compounds. However, since copper(II)oxide (1) has a subnormal magnetic moment (μ = 0.78 BM)

and the μ_4-oxo complexes have normal moments (μ = 1.8 - 2.2 BM) (10, 17), the same type of generalization cannot be made for compounds, such as these two, where a π-interaction has been ruled out.

The structure of the cobalt trimer provided some interesting features. The trigonal prismatic coordination of the central cobalt(II) atom provided the first example of this type of coordination where oxygens were the donor atoms. All other known examples of discrete trigonal prismatic complexes were complexes of the dithiolate ligand (47). After this structure was completed, a trigonal prismatic complex with a sexadentate ligand using nitrogen atoms as donors was reported (48). At this time there are three different types of complexes--complexes of bidentate, tridentate and a sexadentate ligands--showing trigonal prismatic coordination. The fact that none of these show large distortions from a trigonal prismatic arrangement suggests that there may be a significant energy minimum at trigonal prismatic coordination; the existence of such a minimum has been questioned (47). Further work on similar complexes of 2-aminoethanol are now in progress (63). Replacement of the central cobalt by other metal ions and further spectral and structural studies should provide answers to many of the questions raised by the work on this complex. Horrocks (64) is presently investigating the magnetic anisotropy of this complex.

APPENDIX

The following unpublished fortran program to calculate the best least-squares plane for a set of atoms was written with the help of Dr. J. A. Bertrand for the Univac 1108 computer.

```
C      THIS PROGRAM TRANSFORMS AXES TO AN ORTHOGONAL SET,CALCULATES THE
C      BEST LEAST SQUARES PLANE FOR A SET OF N ATOMS, AND CALCULATES
C      THE DISTANCE OF EACH ATOM FROM THE PLANE (IN ANGSTROMS)
C      POSITIVE DISTANCES FROM THE PLANE ARE OPPOSITE THE ORIGIN
C      THE COORDINATES IN THE CALCULATED PLANE ARE REAL,NOT FRACTIONAL
C      X(I),Y(I),ANDZ(I) ARE REAL COORDINATES IN THE ORTHOGONAL SYSTEM
C      P(I) IS THE DISTANCE OF THE ATOM FROM THE CALCULATED PLANE
       DIMENSION X(20),Y(20),Z(20),P(20),WORD(20),TITLE(12)
       DOUBLE PRECISION NUMA,NUMB,NUMC,NUMD,DENOM
       REAL ADP,BDP,CDP,L,M,N,PP,DDP
       IN=5
       III=6
C      READ IN TITLE CARD
       READ (IN,850)(TITLE(I),I=1,12)
  850  FORMAT (12A6)
       WRITE (III,851)(TITLE(I),I=1,12)
  851  FORMAT (1H112A6/)
C      READ IN UNIT CELL DIMENSIONS AND TRANSFORM, SAME FORMAT AS FORDAP
  100  READ (IN,102)A,B,C,ALPHA,BETA,GAMMA
  102  FORMAT (3F10.4,3F10.6)
       WRITE(III,10)
   10  FORMAT(60H       A          B          C      ALPHA       BETA      GAMM
      1A   /)
       WRITE (III,101)A,B,C,ALPHA,BETA,GAMMA
  101  FORMAT (3F10.4,3F10.5/)
       COSA=COS(ALPHA*0.017453)
       COSB=COS(BETA*0.017453)
       COSC=COS(GAMMA*0.017453)
       SINA=SIN(ALPHA*0.017453)
       SINB=SIN(BETA*0.017453)
       SINC=SIN(GAMMA*0.017453)
C      READ IN DATA SET, SAME FORMAT AS ATOM PARAMETER CARDS FOR FLS
  199  I=0
       IFLAG=0
       NORG=0
       WRITE(III,301)
  301  FORMAT (34H ATOMS FOR WHICH PLANE IS DESIRED-/)
       WRITE(III,11)
   11  FORMAT(53H   I   ATOM                X           Y           Z   /)
  200  I=I+1
       READ (IN,201)WORD(I),XX,YY,XP,YP,ZP,ZZ
  201  FORMAT (A6,3X,6F9.6)
       IF (XP-10)300,400,400
C      TRANSFORM TO NEW COORDINATES
  300  X(I)=XP*A+YP*B*COSC+ZP*C*COSB
       Y(I)=(YP*B+ZP*A*SINB*COSA)*SINC
       Z(I)=ZP*C*SINB*SINA
       IF (XP-5)310,320,320
  320  I=I-1
       IFLAG=1
  310  IF (IFLAG-1)311,200,200
  311  CONTINUE
       II=I-1
C      SET UP SUMMATIONS FOR NORMALIZED EQUATIONS
```

```
      SN=FLOAT(I)
      SX=SX+X(I)
      SY=SY+Y(I)
      SZ=SZ+Z(I)
      SXX=SXX+X(I)*X(I)
      SXY=SXY+X(I)*Y(I)
      SXZ=SXZ+X(I)*Z(I)
      SYZ=SYZ+Y(I)*Z(I)
      SYY=SYY+Y(I)*Y(I)
      SZZ=SZZ+Z(I)*Z(I)
      WRITE (III,302) I,WORD(I),XP,YP,ZP
  302 FORMAT(I3,3X,A6,5X,3F12.5/)
      GO TO 200
C     SOLUTION OF NORMALIZED EQUATIONS
  400 IF (ABS(SX).LT.(0.0001)) NORG=1
      IF (NORG) 402,402,450
  402 DENOM=SXX*SYY*SZZ+SXY*SYZ*SXZ+SXZ*SXY*SYZ
     1-SXZ*SYY*SXZ-SXY*SXY*SZZ-SXX*SYZ*SYZ
      NUMA=SZ*SYY*SXZ+SY*SXY*SZZ+SX*SYZ*SYZ-SX*SYY*SZZ-SZ*SXY*SYZ-SY*SXZ
     1*SYZ
      NUMB=SXX*SZ*SYZ+SXY*SX*SZZ+SY*SXZ*SYZ-SZ*SXY*SXZ-SX*SYZ*SXZ-SY*SXX
     1*SZZ
      NUMC=SY*SXX*SYZ+SZ*SXY*SXY+SX*SYY*SXZ-SX*SXY*SYZ-SY*SXY*2XZ-SZ*SXX
     1*SYY
      ADP=NUMA/DENOM
      BDP=NUMB/DENOM
      CDP=NUMC/DENOM
      XM=1.0
      XM=SIGN(XM,CDP)
      PP=(SQRT(1.0/(ADP*ADP+BDP*BDP+CDP*CDP)))*XM
      L=(ADP)*PP
      M=(BDP)*PP
      N=(CDP)*PP
      GO TO 490
  450 DENOM=SYY*SZZ*SN+SYZ*SZ*SY+SY*SYZ*SZ-SY*SZZ*SY-SYZ*SYZ*SN-SYY*SZ
     1*SZ
      NUMB=SY*SZZ*SX+SYZ*SXZ*SN+SXY*SZ*SZ-SXY*SZZ*SN-SYZ*SZ*SX SY*SXZ*
     1SO
      NUMC=SY*SXZ*SY+SXY*SYZ*SN+SYY*SZ*SX-SYY*SXZ*SN-SXY*SZ*SY-SY*SYZ*SX
      NUMD=SXY*SZZ*SY+SYZ*SYZ*SX+SYY*SXZ*SZ-SYY*SZZ*SX-SYZ*SXZ*SY-SXY*
     1SYZ*SZ
      BDP=NUMB/DENOM
      CDP=NUMC/DENOM
      DDP=NUMD/DENOM
      XM=1.0
      XM=SIGN(XM,DDP)
      L=-(SQRT(1.0/(1.0+BDP*BDP+CDP*CDP)))*XM
      M=BDP*L
      N=CDP*L
      PP=(DDP)*L
  490 WRITE (III,401)L,M,N,PP
  401 FORMAT (25H EQUATION OF THE PLANE IS//F9.5,4H X+ F9.5,4H Y+ F9.5,
     14H Z+ F9.5,4H = 0/)
C     CALCULATION OF DISTANCE OF EACH POINT FROM BEST PLANE
      WRITE(III,12)
   12 FORMAT(64H  I    ATOM              X(I)          Y(I)          Z(I)
     1  P(I)  /)
      IMAX=I-1
      I=0
  500 I=I+1
      P(I)=L*X(I)+M*Y(I)+N*Z(I)+PP
      WRITE (III,501) I,WORD(I),X(I),Y(I),Z(I),P(I)
  501 FORMAT(I3,3X,A6,5X,4F12.5/)
      IF (I-IMAX)500,600,600
  600 IF (XP-20)700,800,800
C     CLEAR SUMMATIONS FOR NEW CALCULATION
  700 SX=0
      SY=0
      SZ=0
      SXX=0
      SYY=0
      SZZ=0
      SXY=0
      SXZ=0
      SYZ=0
      GO TO 199
  800 WRITE (III,801)
  801 FORMAT (20H END OF CALCULATION )
      END
```

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